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Electrodialytic Recovery of Organic Acids from Kraft Black Liquor and Analysis with HPIC

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Affidavit

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly indicated all material which has been quoted either literally or by content from the sources used. The text document uploaded to TUGRAZonline is identical to the present master's thesis.

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Abstract

Kraft black liquor is an aqueous process stream containing valuable compounds like cooking chemicals, lignin, organic acids and degradation products of wood carbohydrates. Due to the rising demand for substitutes for fossil fuel-derived chemicals, one major goal of this thesis is to set up an electrodialysis apparatus for the simultaneous removal of cooking chemical and organic acids from black liquor. Additionally, a high-pressure anion-exchange chromatography with two different detection methods, suppressed conductivity detection and pulsed amperometric detection, was commissioned. Pulsed amperometric detection can be used to analyze sugars associated with wood. Suppressed conductivity detection is used for the analysis of inorganic and organic acid anions.

Proof of concept experiments for the bipolar electrodialysis were performed with a model solution, imitating the properties of black liquor. Subsequently, experiments with diluted black liquor from a local paper mill were carried out. During all experiments pH shifts indicated the accumulation of acid and base in the referring compartments. The pH value in the salt compartment decreased by 0.25 pH units when experiments were conducted using black liquor model solution. However, with diluted black liquor they did not change. This is most likely due to buffering effects of lignin. The electric power of the electrodialysis cell was monitored over time. With the model solution the power increased by 3 W and 8 W over time because of decreased resistance caused by temperature increase and subsequent increase of ion mobility. However, with diluted black liquor the power decreased by 7 W and 5.5 W over time. This might be the result of increased resistance caused by lignin deposition on the surface of the ion-exchange membranes.

Acid accumulation and depletion were monitored using ion chromatography. Experiments with black liquor model solution showed accumulation of lactate, acetate and formate in the acid compartment. In the salt compartments the respective concentrations decreased. Among the organic acid anions, formate accumulated the fastest with a rate of 18 mg/(L min). Experiments with black liquor showed minor lactate and acetate accumulation in the acid compartment. Formate concentration increased by around 200 mg/L. This refers to a rate of 3.5 mg/(L min). Lactate and acetate might be more prone to adsorption on the lignin layer deposited on the membranes.

In future experiments lignin removal from the feed stream prior to electrodialysis should be considered to prevent fouling a priori.

Zusammenfassung

Schwarzlauge aus dem Kraft-Prozess enthält neben den Kochchemikalien auch Lignin und Abbauprodukte von Cellulose und Hemicellulose wie organische Säuren. Vor allem die Isolierung von organischen Säuren könnte zukünftig eine alternative Quelle zu erdölbasierten Chemikalien bieten. Ein möglicher Prozess organische Säuren und Kochchemikalien gleichzeitig aus der Schwarzlauge abzutrennen ist die bipolare Elektrodialyse, die in dieser Arbeit untersucht wird. Zusätzlich wird eine Hochdruckionenchromatographie mit supprimierter Leitfähigkeitsdetektion bzw. gepulster amperometrischer Detektion in Betrieb genommen. Die amperometrische Konfiguration bietet die Möglichkeit Zucker, die typischerweise in Holz und damit assoziierten Prozessströmen gefunden werden, zu bestimmen. Supprimierte Leitfähigkeitsdetektion wird zur Analyse von anorganischen und organischen Ionen eingesetzt.

Erste Versuche zur elektrodialytischen Aufarbeitung von Kochchemikalien und organischen Säuren wurden mithilfe einer Modelllösung, die die Eigenschaften der Schwarzlauge so gut wie möglich imitiert, durchgeführt. Die nachfolgenden Experimente wurden mit verdünnter Schwarzlauge einer örtlichen Papiermühle durchgeführt. Während der Versuche wurde der pH-Verlauf in allen Kammern bestimmt. Wie erwartet sank der pH-Wert im Säurebehälter und stieg im Laugebehälter. Der pH-Wert der Salzlösung sank bei Elektrodialyse der Modelllösung um 0.25 pH-Einheiten, veränderte sich aber im Falle der verdünnten Schwarzlauge nicht. Diese Beobachtung kann auf die Pufferwirkung des enthaltenen Lignins zurückgeführt werden. Während der Experimente wurde außerdem die elektrische Leistung der Anlage überwacht. Im Falle der Modelllösung stieg die Leistung um 3 W und 8 W bis ein Plateauwert erreicht war. Vermutlich wir das durch den sinkenden Widerstand aufgrund der erhöhten Ionenbeweglichkeit, hervorgerufen durch den Temperaturanstieg in der Flüssigkeit, verursacht. Mit verdünnter Schwarzlauge hingegen fiel die Leistung mit der Zeit um 7 W und 5.5 W ab. Wahrscheinlich lagert sich Lignin an den Ionenaustauschmembranen ab und erhöht so den Widerstand.

Die Säurebildung bzw. Anionenabreicherung wurde mittels Ionenchromatographie bestimmt. Für die Modelllösung war ein deutlicher Anstieg der Laktat-, Azetat- und Formiatkonzentrationen im Säurebehälter zu sehen. Im Salzkreislauf wurde die entsprechende Abreicherung festgestellt. Unter den organische Anionen war die Anreicherung von Formiat mit einer Rate von 18 mg/(L min) am größten. Experimente mit verdünnter Schwarzlauge zeigten nur wenig Anstieg der Laktat- und Azetatkonzentration. Die Zunahme an Formiat im Säurekompartment war noch am größten mit einer Rate von 3.5 mg/(L min). Eventuell sind Laktat und Azetat anfälliger für Adsorption an der Ligninschicht auf der Membran als Formiat.

Für zukünftige Experimente sollte erwogen werden Lignin möglichst vollständig zu entfernen um ein Fouling dadurch von vornherein auszuschließen.

Contents

1 Introduction and Motivation

Black Liquor is an aqueous process stream of the Kraft pulp and paper production [1], which contains various valuable components like cooking chemicals, lignin and degradation products of wood carbohydrates such as organic acids [2–4]. Except for lignin, all other organic constituents are present at low concentrations. However, sugars and organic acids are much more interesting as substitutes for fossil fuel-derived chemicals [4–6].

The goal of the present work was to provide basics for future research activities, dealing on the one hand with the analysis of inorganic and organic components of black liquor using ion chromatography. On the other hand, a feasibility study on the electrodialytic recovery of organic acids and alkaline cooking chemicals was carried out.

The first part of the thesis covers the commissioning of a high-pressure anion-exchange chromatography combined with two different analytical columns and two different detectors. A CarboPac PA20 column combined with a pulsed amperometric detector enables the separation and subsequent analysis of low-molecular-mass sugars. For the simultaneous determination of inorganic anions and organic acid anions, suppressed conductivity detection was set up. These analytes are separated using an IonPac AS11-HC column upstream to the conductivity detector. Furthermore, a suitable sample preparation procedure including a solid phase extraction step was developed for the organic acid determination from black liquor. Trouble shooting for both ion chromatography configurations was performed and is explained in detail.

The second part of this work deals with the set-up of a recovery system of the organic acids and the cooking chemicals from black liquor. A pilot-scale electrodialysis apparatus was used to enrich negatively charged organic acid anions and positively charged sodium cations in different compartments of the plant. Proof of concept experiments were conducted using a model solution, having a composition similar to black liquor. In the last part of the thesis, electrodialytic recovery of the above mentioned ions from diluted black liquor was performed. During all experiments, voltage, current and the resulting power were monitored. Simultaneously, samples were withdrawn to determine their pH value, conductivity and acid content.

In the present work, all requirements to perform experiments on the electrodialytic recovery of organic acids and cooking chemicals from black liquor and similar process streams were accomplished and demonstrated to work using suitable test solutions or diluted black liquor.

2 Theoretical Background

Kraft pulping is the most commonly used process for pulp fabrication [7]. A simplified process scheme of the Kraft process can be seen in figure 2.1.

The aim is the disintegration by degradation and subsequent solubilization of lignin, which holds the wood fibers together and stabilizes the wood's structure [8]. Cooking the wood chips at high temperature using a cooking liquor, the so called white liquor, results in liberation of the cellulose fibers which can be further processed to paper or board [8, 9]. White liquor is an aqueous sodium hydroxide and sodium sulfide solution [9]. The spent cooking liquor is called black liquor [6, 8–10]. This is due to its dark brown color, which results from dissolved wood constituents and their degradation products [9]. However, it might also be seen as a pictorial description for its highly complex composition.

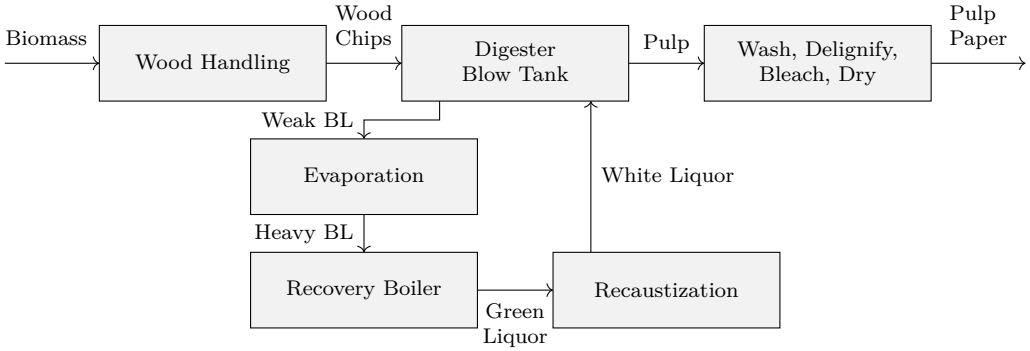

Figure 2.1: Simplified flowchart of the Kraft pulping process, adapted from [11].

Black Liquor is an odoriferous mixture containing hundreds of different compounds [5, 8, 12]. The exact composition of Kraft black liquor varies considerably, depending on the process conditions and the raw materials used [2, 3, 8]. During the Kraft process, approximately half of the wooden raw material gets dissolved in the black liquor [7,13]. The main components found in black liquor are sodium salts and sulfur compounds (e.g. NaOH, Na_2CO_3, Na_2S, Na_2SO_4 and organic Na salts [14]), lignin and degradations products resulting from the breakdown reactions of the wood carbohydrates, cellulose and hemicellulose [5–8, 10, 12, 13]. An end-wise degradation reaction, the so-called peeling reaction, causes the polysaccharide degradation and simultaneous formation of various organic acids [2–4].

So far more than 20 different carboxylic acids were identified in black liquor [5]. Aliphatic carboxylic acids found in black liquor are usually classified in volatile acids

(e.g. formic and acetic acid) and non-volatile hydroxy acids (e.g. lactic acid). In addition to that, minor amounts of non-hydroxylated di- and tricarboxylic acids have been identified. [3, 10, 13] The hydroxy acids are further divided in low-molecular-mass hydroxy acids containing two to four carbon atoms and high-molecular-mass hydroxy acids with five or six carbon atoms. The latter form intramolecular esters (i.e. lactones) when liberating them from their sodium salts. [5, 10]

The concentrations of the identified acids vary with respect to the type of raw material and delignification method [2]. Data collected from different publications can be found in table 2.1. In softwood black liquor formic, acetic, oxalic, glycolic, glucoisosaccarinic acid (GISA), xyloisosaccarinic acid (XISA), malic, lactic, 3,4-dideoxypentonic, 2-hydroxyglutaric, succinic, 4-hydroxybutanoic, 2-hydroxybutanoic acid (HBA), 2-hydroxy-4-pentenoic, methylsuccinic, 2,5-dihydroxypentanoic acid (DHPA) and 2-hydroxy-2-methylbutanoic acid were identified [3, 4, 6]. Birch and aspen black liquors contained the same acids with one exception: 2-hydroxy-2-methylbutanoic acid was neither found in birch black liquor nor in aspen black liquor. The most abundant non-volatile acids present in softwood black liquor were glucoisosaccharinic, lactic, and 3,4-dideoxypentonic acid. In birch and aspen black liquors the quantitatively most important acids were lactic, 2-hydroxybutanoic, glucoisosaccharinic and xyloisosaccarinic acid. [2, 3, 6, 10]

Traditionally, Kraft black liquor is concentrated and combusted in a recovery boiler to produce heat and recover cooking chemicals [4, 8]. However, organic acids have a low heat value compared to lignin [4, 8, 10, 12]. In fact, two-thirds of the total heat produced by burning the liquor organics are derived from lignin and only one-third comes from the remaining components [10, 13]. Therefore, the partial withdrawal from black liquor and alternative use of organic acids would be an interesting option for pulp mills [8, 10, 13]. A softwood Kraft mill producing 500 000 t of unbleached pulp per year could produce 15 000 t volatile acids, 9000 t low-molecular-mass hydroxy acids, and 20 000 t high-molecular-mass hydroxy acids, if only 20 % of the feedstock material would be withdrawn. The corresponding hardwood Kraft mill would produce 15 000 t of volatile acids, 12 000 t of low-molecular-mass hydroxy acids and 14 000 t of high-molecular-mass hydroxy acids. [10] Globally, the Kraft pulp mills could produce 30 000 000 t of hydroxy acids per year [8].

In general, carboxylic acids can be used as single components or mixtures [10, 13]. Because of the increasing demand in biomass-based substitutes of fossil fuel-derived chemicals, multiple applications in the fine chemicals industry, in polymer production, food and pharmaceutical industry are evident [4–6]. Organic acids can be used as chemical intermediates [12], fermentation feedstocks [12], food additives [5], polymer precursors [5] or heavy metal chelating agents [8]. However, also applications in cosmetics [4, 8] or tissue-engineering [4] are possible. Polymers made from hydroxy acids require high purity as impurities can cause undesired side reactions, catalyst deactivation or termination of chain length increase. However, separating and purifying the single hydroxy acids is often not necessary. Mixtures of hydroxy acids can be copolymerized. [4]

So far, formic, lactic, acetic and glycolic acid are commercially most important.

Table 2.1: Organic acid concentrations in black liquor reported in literature. LA-lactic acid, AA-acetic acid, GA-glycolic acid, FA-formic acid, SA-succinic acid, OA-oxalic acid, HBA-2-hydroxybutanoic acid, DHPA-2,5-dihydroxypentanoic acid, GISA-glucoisosaccarinic acid, XISA-xyloisosaccarinic acid.

LA g/L	AA g/L	GA g/L	FA g/L	SA g/L	OA g/L	HBA g/L	DHPA g/L	GISA g/L	XISA g/L	Ref.
Hardwood										
3.40	-	-	6.50	-	1.14	-	-	2.84	2.55	[2]
4.00	-	-	5.00	-	1.57	-	-	3.75	2.48	[2]
2.63	-	0.77	-	0.21	-	4.54	-	1.92	3.04	[3]
2.60	-	0.69	-	0.24	-	3.45	-	2.75	3.36	[3]
2.8	13.7	1.2	5.4	-	0.5	4.0	1.1	7.3	3.2	[4]
4.00	-	2.00	-	0.22	0.17	7.00	0.90	4.00	4.00	[5]
1.98	11.50	1.02	3.50	-	0.00	4.08	0.00	2.97	3.50	[6]
5.2	39.6	4.5	14.2	-	-	-	-	6.6	6.9	[10]
Softwood										
6.20	-	-	7.00	-	0.85	-	-	10.64	0.78	[2]
4.92	-	1.56	-	0.18	-	0.95	-	7.27	0.43	[3]
4.2	4.4	2.8	5.4	-	0.5	1.3	1.3	15.7	3.7	[4]
4.00	-	3.00	-	0.22	0.13	1.00	1.50	9.00	0.50	[5]
3.45	3.81	1.37	3.85	-	0.00	1.12	0.92	9.06	2.72	[6]
2	5	1	5	-	-	-	-	3	1	[8]
Mixtures of Hard- and Softwood										
4	6	3	12	-	-	-	-	11	5	[8]

The application of high-molecular-mass hydroxy acids has been studied only to a limited extent. [10]

2.1 Ion Chromatography

Ion chromatography (IC) is a well-established analytical technique for the determination of inorganic anions and cations, organic acids and bases as well as amino acids, amines, proteins, glycoproteins, sugar alcohols and carbohydrates [15–19]. It is the method of choice for the rapid analysis of multiple ions in solution. Advantages of IC are small sample volume, high sensitivity (ppb level), relatively easy sample preparation, high selectivity and resolution. [17, 20] The most popular branch of IC is anion-exchange chromatography with suppressed conductivity detection [19, 21]. Therefore, the main focus of this section is on the set-up thereof, together with anion chromatography combined with pulsed amperometric detec-

tion, as these two analytical configurations will be commissioned.

2.1.1 Ion Separation

Charged species and especially inorganic and small organic anions and cations are separated using IC [18, 20]. Two main processes govern the separation behavior in ion-exchange chromatography: On the one hand electrostatic interactions take place, i.e. ion-exchange between analyte ions and the mobile phase as well as the stationary phase. On the other hand hydrophobic interactions occur, among which adsorption is the most important one. [18,19,22] Electrostatic interactions are more effective than hydrophobic ones [20].

Analyte ions or molecules get ionized at very acidic or alkaline pH values resulting from acids or bases used as eluents. Depending on the pK_avalue, the ionic character of an acid and its referring anion changes. Within a certain range, the species becomes more ionic if the difference between the actual pH value and the pK_avalue increases. Consequently, anions with a higher pK_avalue will elute earlier than anions with a lower one, as they are more acidic. Similarly, cations with a lower pK_bvalue will elute after cations with a higher pK_bvalue, as they are more basic. [19]

In anion-exchange chromatography quaternary ammonium ions are used as fixed ions on the support material of the stationary phase. Cation-exchange resins carry sulfonate, carboxyl or phosphonate groups. [17,19,22] Competitive bond formation between the ionic and polar analytes and the functional groups of the stationary phase is the basis of analyte separation in ion-exchange chromatography. The first step of the separation mechanism is the diffusion of an analyte ion close to the functional groups of the resin and bond formation via the Coulomb force F_C (compare formula 2.1). Here q_1 and q_2 are the charges of the two interacting ions, ϵ is the dielectric constant of the medium and r is the distance between the two interacting ions. [19, 22]

$$F_C = \frac{q_1\, q_2}{\epsilon\, r^2} \tag{2.1}$$

To precisely explain the separation mechanism, some thermodynamic principles need to be considered: The Coulomb force between two similar charges is repulsive and attractive between two dissimilar charges. Attractive forces between two oppositely charged ions cause an enthalpy (H) and free energy (G) decrease. Therefore, the process is thermodynamically favored. Analyte ions bound to the column material compete with similarly charged eluent ions for the resin binding sites. Breaking the bond between a negatively charged analyte ion and a positively charged resin ion requires work, i.e. it is not thermodynamically favorable. However, the enthalpy and free energy increase is more than compensated by the decrease in free energy and enthalpy due to the binding of negatively charged eluent ions to the positively charged resin ion. This is due to the fact that the concentration of the eluent is much higher than the concentration of the analyte. Typically, the eluent concentration ranges from 10 mmol/L to 100 mmol/L. The analyte concentration

is in the range of µmol/L or even lower. As the eluent concentration is 1×10^4 to 1×10^5 times higher than the analyte concentration, the energy required to displace an analyte ion from the stationary phase is much lower than the energy released by the binding of the analyte ion to the stationary phase. This results in an overall decrease of the free energy. Therefore, the chromatographic separation in total is thermodynamically favored. [19]

The strength of the bond between the analyte ions and the resin ions determines the analyte retention. It depends mainly on the charge of the ion, its size, the polarisability and the degree of adsorption, i.e. the hydrophobicity of the ion. [17, 19, 20, 22]

Monovalent ions are less tightly bound to the stationary phase than divalent ones. Consequently, the elution of a divalent ion from the resin requires a higher eluent concentration. To explain the possibility of separating several monovalent ions from each other, concepts other than the Coulomb force have to be considered. This is due to the fact that the Coulomb force assumes charges to be concentrated at the center point of an ion. This however, is an assumption which is not applicable in ion chromatography. The charge density on the ion surface is the investigated quantity, rather than the charge itself. This means that bulky ions elute earlier than small ions of the same valency. [19]

The thickness of the hydration shell, being approximately proportional to the charge density, also affects the separation process. Small ions with a high charge density have a thicker hydration shell than large ones with a low charge density. To bind to the resin, ions need to free themselves from the hydration shell. This causes an increase in the free energy G. Binding to the stationary phase decreases G, unbinding the ion from the stationary phase increases G again and the formation of a new hydration shell around the freed ion decreases G. The overall change of G is the sum of all these steps. The reduction in free energy G is larger for small ions with a thicker hydration shell than for ions with a lower charge density and a thinner hydration shell. Therefore, smaller ions are eluted earlier from the column. [19]

Ions containing oxygen atoms, as it is the case for the bulky acetate, can form very stable hydration shells as strong hydrogen bonds are formed between the oxygen atom and hydrogen atoms of water. This additional effect causes the free energy to decrease more than expected based on the charge density of acetate. As a result, acetate and other ions of this type elute earlier than e.g. the smaller chloride or bromide ions. [19]

Due to all these influencing factors it is often necessary to empirically develop separation methods for mixtures of multiple ions. However, this is often time consuming. Therefore, much interest is directed towards suitable mathematical retention models allowing prediction of retention times for a wide range of eluent compositions and hence provide computer-assisted optimization of eluent composition. Semi-empirical methods for retention modeling seem to be the most useful ones. An example for commercially available software is DryLab from LC Resources. ANNs (Artificial Neural Networks) are able to predict IC retention data based on a training of a small set of experimental retention data. [20] Simulation and optimization

of separation processes of various ionic species on numerous column types can also be performed with the program Virtual Column® [18].

2.1.2 Eluents in Ion Chromatography

Diluted acids, alkali or salts are typically used as eluents in IC. The addition of organic solvents is also possible, provided that the column material tolerates it. [19] Common eluents in anion chromatography are sodium carbonate/sodium bicarbonate [17, 23–25], borate [24], hydroxide [17, 24] and sodium carbonate/sodium bicarbonate/acetone [26]. In cation-exchange chromatography commonly diluted mineral acids like HCl, HNO_3 and H_2SO_4 are used [17].

The addition of organic solvents can modify the mobile phase, such that adsorption onto the stationary phase is minimized and retention time of more hydrophobic analytes is reduced [18]. Improvement of the separation, the peak shape and the resolution are also reported [19, 27]. In the early 1990s Morris and Fritz recognized that the addition of short aliphatic alcohols such as methanol, ethanol, propanol or butanol to aqueous eluents increases the chromatographic resolution of carboxylic acids dramatically [27].

Hydroxide is especially favorable to be used with suppressed conductivity detection, as the suppression product is water. This gives the lowest possible background signal in conductivity detection. Furthermore, the minimal water dip and the good resolution of weakly bound ionic species are advantages of hydroxide eluents. [16, 17, 19, 21, 24, 28, 29] Compared to carbonate eluents the baseline noise as well as the limit of detection (LOD) are decreased with hydroxide. In addition to that, calibration functions are linear over a wider concentration range than it is the case with carbonate. [29] However, hydroxide has the disadvantage that carbon dioxide present in the air is easily dissolved [17, 27, 29]. Within 12 h the background conductivity of an eluent exposed to the atmosphere doubled, from 1.5 µS to 3 µS [27]. Manual eluent preparation is especially prone to the introduction of carbonate impurities. If carbonate is present in hydroxide eluents baseline shifts during gradient elution, unreproducible retention times and increased detection limits may be the consequence. As carbonate is a stronger displacing ion than hydroxide also broad and asymmetric peak shapes can occur. Hence, electrolytic eluent generators producing high purity hydroxide are used to circumvent manual eluent preparation. [16, 21, 27–29] Additionally, user involvement is reduced as ultrapure water is the only pumped phase in IC [28, 29].

In eluent generation systems water is fed to the electrolysis cell and e.g. potassium counter ions are transported charge-selectively from an external supply cartridge via a cation-exchange membrane into the eluent line. Simultaneously, water electrolysis is performed. H^+ is exchanged with potassium, and hydroxide and potassium give a pure potassium hydroxide solution. [20, 21] Carbonate contamination is therefore limited to a minimum [20], as only ultrapure water is exposed to air. Hence, degassing and selective CO_2 removal is performed prior to the injection valve. This is important in IC as the uptake of CO_2 in water can be up to 1000 ppm to 2000 ppm,

depending on the temperature. The following equilibrium applies: [21]

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{2.2}$$

The removal of anionic impurities from the eluent can be performed using strong anion trap columns being installed in the eluent flow path. These columns, however, have limited capacity. To overcome this limitation continuously regenerated electrolytic trap columns can be used. A continuously regenerated anion trap column (CR-ATC) can be applied to remove anionic impurities from the water used to prepare the eluent. Active removal of carbonate from the column effluent is also possible. This is typically done after the suppressor and before the detector. [21]

To avoid as many impurities as possible the quality of the ultrapure water has to be considered. The eluent quality directly affects the limits of quantification (LOQ) and detection (LOD). For conductivity detection as well as for pulsed amperometry detection it is necessary that the resistivity of the ultrapure water is greater than 18.0 MΩ cm, similar to UV-transparent water required for UV-detection in liquid chromatography. [30]

2.1.3 Instrument Set-Up

An IC system resembles an HPLC system. It consists of a pump module, an injection valve fed by an autosampler, a column oven with a column, a detector module and a data analysis system with appropriate software. The use of alkaline or acidic eluents makes it necessary to construct the entire flow path and chromatographic modules of inert, metal-free materials. Polymers like polyether ether ketone (PEEK) or polytetrafluorethylene (PTFE) are often the materials of choice. [19, 21–23, 31]

Injection Valve

Samples are introduced into the system either by manual injection or by an autosampling device.

Independent of the way of introduction, the sample is filled into the sample loop of the injection valve. Usually 6-way valves are used. While this is done the injection valve has to be in the "Load" position. To inject the sample onto the column the injection valve has to be switched from the "Load" position to the "Inject" position. The volume of the sample loop is typically in the range between 10 µL and 250 µL. [19, 22] However, this depends on the column capacity and the sample concentration.

Stationary Phase - Column

The stationary phase is the heart of the chromatographic system. The choice of a suitable column together with the chromatographic conditions determine the quality of the analysis. [22]

Organic polymers like polyvinyl, polymethacrylate, styrene-divinylbenzene copolymers and ethylvinylbenzene-divinylbenzene copolymers are typically used as column materials [17]. This is due to the fact that organic polymers are more resistant to extreme pH values. Classical HPLC resins such as silica-based materials can only be used in a pH range from 2 to 8. Ion-exchange resins, however, are stable in the highly alkaline region too. [22]

In the majority of cases a guard column is installed upstream to the analytical column to protect the analytical column from contaminants and thereby increase its lifetime [19].

During the analysis, temperature and pressure within the chromatographic system are controlled. Ion chromatography is usually performed at ambient or close to ambient temperature. This is due to the temperature dependence of the dissociation constants of the analytes. As $pK_a$and pK_bvary with temperature, the retention times of analytes that are not fully ionized can vary slightly with temperature. Fully ionized analytes are not affected. The pressure dependence of the dissociation constants is negligibly small. However, pressure fluctuations would negatively influence the chromatographic performance. Additionally, the flow rates of the system are chosen such that diffusion of ions is possible and that the columns are operated in their optimum pressure range. Typical flow rates are between 0.3 mL/min and 2 mL/min. However, this depends on the column dimensions. Higher flow rates can cause incomplete binding and desorption from the column. [19]

Suppressed Conductivity Detection

The choice of detector is based on the type of analytes that are to be detected [19]. In IC detectors are classified in electrochemical ones and light-based ones. Conductivity detection, amperometry and potentiometry belong to the electrochemical detection methods. UV/Vis absorbance, indirect photometry, fluorescence, chemiluminescence and refractive index detection are light-based methods. [20–22,25,26,32] The main focus will be on suppressed conductivity detection (sCD) as well as pulsed amperometric detection (PAD), as these two detection systems will be commissioned.

The most popular detector in IC is the conductivity detector. It can be operated with or without suppressor. [19, 22] Conductivity detection is commonly used in anion chromatography to detect inorganic anions or organic acid anions [19].

The basic principle of conductivity detection is the following: A constant voltage is applied between two electrodes, where the column effluent flows through. As the effluent contains ions, a current is generated. [19] The current is directly proportional to the conductivity of the solution [19, 32]. Equation 2.3 shows the dependency of the conductance C_{elec} on the specific conductance κ and the cell constant K_{cell} [21].

$$C_{\text{elec}} = \frac{\kappa}{K_{\text{cell}}} \tag{2.3}$$

The magnitude of K_{cell} depends on the cell geometry. The specific conductance κ is proportional to the electrolyte concentration c and the molar conductivity Λ_{m}, following the Kohlrausch law (compare formula 2.4). Conductivity detection is analyte specific as κ depends on Λ_{m}. Λ_{m} itself is a function of the ion mobility in solution in the presence of an electric field and hence diffusivity. As ion mobility increases with increasing temperature, it is of utmost importance to control the temperature of the detector during analysis. [21]

$$\Lambda_{\text{m}} = \frac{\kappa}{c} \tag{2.4}$$

Suppressors are aimed to reduce the background conductivity of the eluent and to convert analyte ions into a more conductive form. In other words: using a suppressor increases the signal-to-noise ratio of the conductivity detector. [16, 17, 19, 21, 22] The signal-to-noise ratio directly affects the LOD and the LOQ, causing increased detection and quantification sensitivity [19]. In suppressed conductivity detection, the baseline conductivity, i.e. the noise, is typically below 0.5 nS using strong acids or bases, whereas in unsuppressed conductivity detection the baseline conductivity is around 10 nS [19, 32]. Furthermore, in gradient elution the baseline does not change, which is the case in unsuppressed conductivity detection making the peak area or height determination less accurate [19]. Basically, two suppressor types exist: chemically regenerated suppressors and electrolytically regenerated suppressors [21]. Chemical suppression and generally the concept of suppressed conductivity detection was introduced by Small et al. in 1975 [33]. However, electrolytic suppression is commonly used nowadays [19]. As an electrolytically regenerated suppressor will be commissioned, only this type is explained in detail.

Electrolytically regenerated suppressors rely on the electrolysis of water to generate ions for suppressor regeneration. A voltage of greater than 1.5 V is required for the following half reactions to take place at the anode and cathode of the suppressor: [32]

$$\mathrm{H_2O} \longrightarrow 2\,\mathrm{H^+} + \frac{1}{2}\,\mathrm{O_2}\uparrow + 2\,\mathrm{e^-} \tag{2.5}$$

$$2\,\mathrm{H_2O} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{OH^-} + \mathrm{H_2}\uparrow \tag{2.6}$$

Figure 2.2 shows a scheme of an electrolytically regenerated suppressor downstream to an anion-exchange column. Depending on the eluent the analyte anion $\mathrm{X^-}$ has either a $\mathrm{Na^+}$ or $\mathrm{K^+}$ counter ion. After being eluted from the column the analyte enters the suppressor central chamber, which is enclosed by two cation-exchange membranes (CEM). Only positively charged species can be transported across this type of membrane in presence of an electric field. The cathode and the anode chambers are located to either side of the eluent chamber. Water is pumped into both of these chambers and water electrolysis as shown in formula 2.6 takes place. [19] $\mathrm{H^+}$ ions are transported via the cation-exchange membrane into the eluent chamber and $\mathrm{Na^+}$ or $\mathrm{K^+}$ ions cross the other cation-exchange membrane and enter the

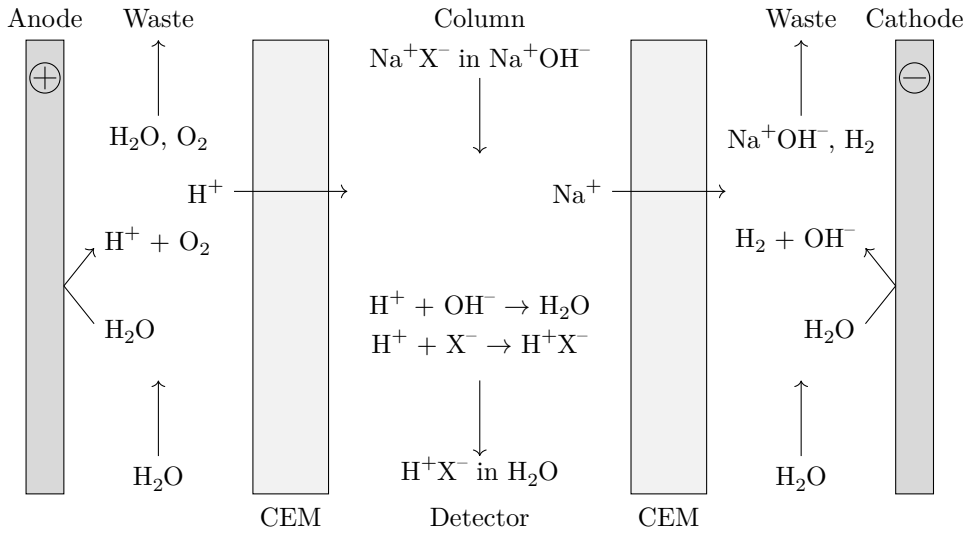

Figure 2.2: Working principle of an electrolytically self-regenerated suppressor. Reproduced from [19]. CEM stands for cation-exchange membrane.

cathode compartment [19, 34]. In the eluent chamber both, OH^- ions and analyte ions bind to an H^+ ion and form either water or the acid form of the analyte. This acid/water mixture leaves the suppressor and enters the detector. In the cathode compartment either sodium hydroxide or potassium hydroxide is formed. Suppressors for cation-exchange chromatography use anion-exchange membranes instead of cation-exchange membranes. [19] At 100 % current efficiency one can easily calculate the required current in A to suppress the conductivity of a certain eluent concentration. The referring correlation is shown in formula 2.7. Here, F is the Faraday constant in C/mol, c is the eluent concentration in mol/m^3 and $\dot{V}$ is the eluent flow rate in m^3/s. [32]

$$I = F\, c\, \dot{V} \tag{2.7}$$

Usually the ion-exchange membranes of electrolytically self-regenerating suppressor have a dynamic capacity in the range of a few hundred µmol/min. For most eluents this is adequate. However, if the concentration of analyte counter ions is high this is not the case. This means that if large sample volumes of trace anions in concentrated base are injected, the dynamic capacity of the suppressor is exceeded. Special operation modes like passing the sample multiple times through the suppressor or the so called “park and neutralize” application can circumvent this limitation. During the latter method the sample is held back in the suppressor and adequate current is supplied. [32]

Operating the suppressor in the recycle mode is the simplest way since the cell effluent can be used to supply water needed for the electrolysis. If the IC is operated with eluent containing organic solvents the recycle mode cannot be used as this

would lead to solvent oxidation at the electrode. The external water mode has to be used. In this mode the transport of solvent molecules from the eluent chamber to the electrodes and resulting reactions at the electrode are significantly reduced. [32]

Pulsed Amperometric Detection

Pulsed amperometric detection was introduced in the early 1980s [22, 35, 36]. It allows the sensitive and selective detection of carbohydrates and other oxidizable species such as amines, sulfur compounds, amino acids, aminosaccharides, peptides and alditols [19,22,35–43]. Detection of sugar even at the pmol level is possible [43]. Generally amperometric detection is used for analytes with a p$K_a$above 7, as such compounds cannot or only hardly be detected by conductivity detection due to their low dissociation. [22]

Generally, amperometric detectors consist of a working electrode (Au or Pt), a reference electrode and a counter electrode. At the working electrode either an oxidation or a reduction reaction takes place. The required potential is applied to the working electrode. The reference electrode is usually a Ag/AgCl electrode. In this electrode, a sparingly soluble salt contributes to the electrode reaction as a second solid phase in addition to the element and the electrolyte. Thus, the activity of the potential-determining cation depends on the activity of the anion involved in the formation of the sparingly soluble salt, by the solubility product. Ag/AgCl electrodes are preferably used because of their constant potential at current flow. The counter electrode has the purpose to maintain the potential. Additionally, it prevents a current flow at the reference electrode, which could destroy it. It is often made from carbon, platinum or gold. [22, 40, 44] Amperometric detectors are flow-through detectors. This means that an electroactive analyte is detected when it passes the detector cell. Partial oxidation or reduction of the species is performed resulting in an anodic or cathodic current. [22,35,44] The analyte oxidation current is integrated and the resulting charge (in C) is proportional to the rate of oxidation reaction [35], which is proportional to the analyte concentration. This signal can be represented in a chromatogram. [22,44] Pulsed amperometric dection is distinguished from amperometry with constant working potential. Integrated pulsed amperometry (IPAD) is a variant of PAD, which shows especially low baseline disturbances caused by pH gradients, solvent gradients, ionic strength variations or metal oxide formation. [22]

Technically, the arrangement of the electrodes in a detector suitable for PAD is solved as follows: The detector consists of two blocks separated by a spacer. One of the blocks houses the reference electrode and the capillary connections. The other block houses the working electrode. Due to this simple arrangement the working electrode can be easily replaced if necessary. Two stainless steel connectors at the inlet and outlet boreholes serve as counter electrode. [22]

Sugar molecules behave as weak acids [36, 37, 40]. Consequently, in alkaline solutions sugars as well as amino acids behave as weak anions [36, 39, 43]. This property renders high-performance anion-exchange chromatography using alkaline

mobile phases a suitable separation method and PAD an appropriate detection method. [36–40, 43]

Electrocatalytic oxidation at the gold working electrode in alkaline media is the detection principle [36]. Hydroxyl- or aldehyde groups of carbohydrates or amino groups of amino acids are oxidized at the surface of the gold electrode when a suitable potential is applied [39]. Applying a voltage and the presence of an electrolyte makes the commonly considered inert noble metals like Au or Pt electrochemically active [40], so that they can catalyze the oxidation reaction. [36] At gold electrodes a pH equal to 12 or higher is necessary for the detection of carbohydrates and polyalcohols [37, 40]. However, the use of gold electrodes has the advantage that detection without simultaneous reduction of oxygen is possible [37, 40]. Pt gives a cathodic response to dissolved O_2. Therefore Au electrodes are more sensitive than Pt ones. [37]. However, the technique cannot distinguish between different types of carbohydrates in a mixture. Therefore PAD is a general detector for carbohydrates and needs to be combined with chromatographic separation prior to detection. [37, 44]

For this detection method it is extremely important that electroactive species do not precipitate on the surface of the working electrode. This would lead to a baseline drift, increased background noise and constantly changing detector response. [22, 37] Carbohydrate detection is especially prone to such behaviour [22]. Therefore, in PAD a potential versus time waveform is repeatedly applied to the working electrode [22, 35]. This waveform consists of different working potentials that are applied at different phases of the waveform [22]. These potentials have different purposes like the electrocatalytic oxidation for detection, followed by oxide formation to clean the electrode surface and oxide reduction to reactivate the electrode. [22, 37, 40] One cycle of the waveform typically takes one second and is repeated with a frequency of one hertz [37]. However, attention has to be paid that the oxidative cleaning step of the waveform is not too aggressive. This means that excessive gold oxide layers cannot be completely reduced to gold during the reactivation step. This leads to passivation of the gold electrode, which results in a detector response decrease. [35, 39] Modern waveforms such as the four-potential waveform developed by Rocklin et al. manage the balancing act between thoroughly cleaning the electrode surface and not recessing it [35].

2.1.4 Basic Peak Shape Interpretation

Chromatographic signals are evaluated by peak area or peak height. Both of them are proportional to the analyte concentration over a wide range. Nowadays, computers with suitable chromatography software are used to provide fully automated sampling, chromatographic separation and signal evaluation. [22]

The chromatographic profile and more precisely the peak shapes give information about the quality of the chromatographic separation. Interactions between the analyte ions, the mobile phase as well as the stationary phase are indicated. Matrix ions interfering with trace level analytes and overloading effects are common

problems in IC and can be identified by interpreting chromatograms. [24] In the following paragraphs some basic principles of evaluating chromatographic profiles are summarized.

Basically, two analyte species can be separated if they spend different time in or at the stationary phase [22, 45]. The retention time difference is desirable and is described by the column selectivity. Large differences in retention time of different species indicate good selectivity of the system. However, also analytes of the same species show slightly different retention. This is due to eddy diffusion, longitudinal diffusion and a delay in mass exchange. This retention time difference is unwanted and is described by the efficiency of a column. If the retention time differences for molecules of the same species are large, the efficiency of the system is bad. Narrow peaks indicate good efficiency. [45]

The retention time is a basic parameter to identify a single component within an analyte mixture [17, 22, 45]. The retention time is determined at the position of the peak top as the analyte concentration is at its maximum there. The gross retention time t_{ms} is the sum of the solute retention time t_{s} and the column dead time t_{m}. The solute retention time is the time a component does not travel along the column and the column dead time is the time an unretained component needs to pass through the column (compare formula 2.8). In chromatograms the components are usually labeled with their gross retention time. [22, 45]

$$t_{\mathrm{ms}} = t_{\mathrm{m}} + t_{\mathrm{s}} \tag{2.8}$$

In a first approximation, the shape of a peak is described by a Gaussian curve [22]. The peak width at the base w_{b} is calculated as the distance between the two inception points of the inflectional tangents and the baseline. Assuming a perfect Gauss peak, w_{b} equals $4\,\sigma$, the fourfold of the standard deviation. As w_{b} is often difficult to determine, w_{h} is more commonly used. w_{h} is the peak width at half of the peak height. The difference in x-direction between the two inflection points equals 2σ. For a perfectly Gaussian peak the referring height is 0.61 times the total peak height h ($0.61\,h$). h is the distance in y-direction from the peak top to the baseline. [45] However, peaks are rarely Gaussian. The degree of peak asymmetry is accounted for using the asymmetry factor A_{s}. [22, 45]

Usually, A_{s} is determined at 10 % of the total peak height h. a is "half" the peak width on the leading side of the peak to the center of the peak and b is "half" the peak width from the center to the tailing side of the peak. The asymmetry factor is calculated according to formula 2.9. [45] If A_{s} is larger than 1 the peak shows so called "tailing". This means a rapid increase of the signal followed by a slow decrease of the signal. If A_{s} is smaller than 1 the peak has a "fronting" or "leading", which means a slow increase of the signal followed by rapid decrease of the signal. If A_{s} equals 1 the peak is symmetric. [22, 45]

$$A_{\mathrm{s}} = \frac{b}{a} \tag{2.9}$$

Tailing is caused by adsorption processes. Fronting is due to an insufficient number of binding sites at the stationary phase, which is the case if the column is overloaded. Hence, some analyte molecules pass the peak center as they cannot bind to the resin. [22] Either volume or concentration overload can happen. Volume overload is caused by too large sample volume. It leads to broad, symmetric peaks that often show flat peak tops even at low analyte concentration. Concentration overload can result in peak fronting, tailing, slit peaks and peaks having secondary humps. [24] As long as the asymmetry factor is between 0.9 and 1.2 the separation column is considered to be good [22]. In case of gradient elution the resulting peaks are always slightly asymmetric with a tailing factor expected to be greater than 1. This is due to the fact that the eluent behind the analyte band has a slightly higher concentration than the concentration necessary to elute the species. The concentration at the front of the band is lower than the eluting concentration. Therefore, the back of the band cannot bind to the resin, but diffuses through the eluent while the front of the band binds to the stationary phase but its diffusion is restricted. [19]

The resolution R_s is the correlation of the column selectivity and its efficiency. It is a measure of how well two components can be separated into different bands. However, the resolution does not provide any information on how broad peaks are. Unresolved peaks can be separated by either increasing the selectivity or the efficiency. At constant temperature, selectivity depends on the specific properties of the sample components, the mobile and the stationary phase used. R_s is expressed as the difference between the gross retention times of the two investigated peaks and the arithmetic mean of their respective peak width at the peak base. The referring formula 2.10 is shown below. [22, 45] In case of a Gaussian peak two completely baseline resolved peaks have a resolution of $R_\mathrm{s} = 2$. At $R_\mathrm{s} = 0.5$ two components can still be recognized as separate peaks. [22] Sufficiently large values of R_s between 1.5 to 2 are aspired. Increasing the resolution can be performed by increasing the tray number, i.e. using a longer column. However, this has some disadvantages like increasing the time required for analysis and increasing the back pressure. Increasing the resolution by increasing the efficiency should be done by decreasing the particle diameter of the resin, as this does not affect the analysis time. [45]

$$R_\mathrm{s} = \frac{t_{\mathrm{ms},1} - t_{\mathrm{ms},2}}{\frac{w_{\mathrm{b},1} + w_{\mathrm{b},2}}{2}} = \frac{2\,\Delta t_\mathrm{ms}}{w_{\mathrm{h},1} + w_{\mathrm{h},2}} \tag{2.10}$$

To get information on the column efficiency the theoretical tray number N and the theoretical tray height H_theor are often determined. The theoretical tray number is a measure for the extent of peak broadening caused by a separation system. It does not provide information on the number of equilibrium stages building up along the column. The height of a theoretical plate is related to the tray number by the length of the separator column L. N and H_theor apply only for the case that isocratic elution is performed. The respective formulas can be found below. [22, 45]

$$H_{\text{theor}} = \frac{L}{N} \tag{2.11}$$

$$N = \left(\frac{t_{\text{ms}}}{\sigma}\right)^2 = 16 \left(\frac{t_{\text{ms}}}{w_{\text{b}}}\right)^2 = 8 \ln(2) \left(\frac{t_{\text{ms}}}{w_{\text{h}}}\right)^2 \tag{2.12}$$

The chromatographic efficiency of a certain peak as a function of the linear flow rate being influenced by longitudinal diffusion, eddy diffusion and mass exchange delay can be described using the van-Deemter equation. In formula 2.13 the correlation for the theoretical tray height H_{theor} according to the van-Deemter theory can be found. In this formula ν is the linear flow rate. The term A characterizes the peak dispersion caused by eddy diffusion, which is independent of the flow rate. B/ν describes the longitudinal diffusion and $C\,\nu$ gives information on the lateral diffusion and the mass-transfer resistance between mobile and stationary phase. However, the validity of the van-Deemter equation for liquid chromatography is limited. [22, 45]

$$H_{\text{theor}} = A + \frac{B}{\nu} + C\,\nu \tag{2.13}$$

By now only measures were discussed for cases where peaks could be undoubtedly recognized as peaks. To decide if an analyte is present within a sample or not requires the determination of a certain concentration limit. LOD, the limit of detection, is the smallest concentration at which the presence of an analyte can be determined qualitatively. This means that the measurement signal, usually the peak height, must be significantly larger than the baseline noise. The limit of quantification, LOQ is the smallest concentration at which an analyte can be quantified and the measured data do not exceed a certain statistical variation limit. [45]

System peaks are normally eliminated in IC by the suppressor. Only the water dip, which is typically a negative peak placed before the analyte peaks, can usually be seen. Under high overloading conditions (e.g. 500 mmol/L NaCl) this dip can become positive as the suppressor is exhausted. [24] Matrix ions having ion-displacing effects can also be problematic. Their presence can cause peak broadening and poor peak separation. [20] The elimination of such unwanted matrix elements often requires special sample preparation methods.

2.1.5 HPIC in Pulp and Paper Industry

In pulp and paper production corrosion is a serious problem. Therefore concentration of chloride, chlorite and chlorate are monitored. Sulfite, sulfate and thiosulfate are by-products of the recovery process and oxalate can form insoluble salts. All these ions are analyzed to monitor the reduction-oxidation environment in the recovery cycle. Oxalate, chlorate, sulfite, sulfate and thiosulfate are determined by conductivity detection and sulfide is measured using pulsed amperometric detection. Interferences from the alkaline sample matrix are removed by neutralization with high-capacity cation-exchange resins. [9]

For the analysis of wood sugars, wood and wood-pulp are generally hydrolyzed in sulfuric acid. The resulting sugar monomers are separated by anion-exchange chromatography and quantified using PAD. Detailed qualitative and quantitative analysis of the present sugars gives information on the pulping conditions. Different levels of arabinose, galactose, glucose, xylose and mannose can be found in pine samples. Fucose is used as internal standard. [46]

Davis et al. discussed chromatographic conditions and critical factors for the analysis of sugars occurring in wood, pulp and other lignocellulosics. Sulfuric acid hydrolysis is required for the compositional analysis of lignocellulose. After this step some researchers neutralize the samples and remove sulfate prior to analysis, while others omit these steps. A major difficulty in wood sugar analysis is the resolution of hemicellulosic sugars like arabinose, galactose and rhamnose, while xylose and mannose are well resolved. However, Davis et al. managed to resolve rhamnose from xylose and mannose. Additionally, they detected glucose, galactose and arabinose. Fucose was used as internal standard. In line-solid phase extraction was performed to remove hydrophobic substances that have the potential to foul the analytical column. Lignin is one of these compounds. [38]

Kraft black liquor is a very complex and difficult sample matrix. Qualitative as well as quantitative analysis of the low-molecular-mass aliphatic carboxylic acids as their carboxylate anions together with chloride, sulfate and thiosulfate was performed by ion chromatography with suppressed conductivity or suppressed electrospray ionisation mass spectrometry detection (ESI-MS). Chloroacetate and phosphate were used as internal standards. Peaks of glucoisosaccharinate, xyloisosaccharinate, 3,4-dideoxy-pentonate, 2-hydroxy-4-pentenoate and deoxy-tetronate anions could only be identified with the IC-ESI-MS detection due to a lack of commercially available standard chemicals. With the IonPac AS11-HC column it was not possible to separate the following coeluting anions: 2-deoxy-tetronate and 3-deoxy--tetronate, α-glucoisosaccharinate and β-glucoisosaccharinate, acetate and glycolate, malate and succinate. [2]

Samples being in an unsuitable physical state or showing a sample matrix that interferes with the analysis need to undergo sample preparation procedures [17]. Some of these techniques are necessary for practically all samples, whereas others are quite outlandish.

Common pretreatment techniques applied to liquid samples are filtration, dilution, pH adjustment, derivatization, liquid-liquid extraction, solid phase extraction (SPE), microdiffusion and membrane separation (dialysis/ultrafiltration). Solid samples are often dried, homogenized, dissolved, extracted/leached, digested, ashed or combusted. To measure gaseous samples with IC they have to be absorbed in a liquid or solid phase or chemically converted. [17]

To prevent fouling of the column, capillary tubing, frits and other hardware, it is necessary for all types of liquid chromatography to remove particulate matter from the samples. Even though many samples (e.g. water samples) are obtained in a form that might appear to require no further treatment prior to injection, all samples have to be filtered through a membrane filter of porosity 0.45 µm or less.

However, disposable filter units were observed to release contaminants from the filter membrane. [17,47] Rinsing with ultrapure water prior to sample filtration and disposing the first few mL of the sample is recommended [17].

Adjusting the pH value of very acidic or alkaline samples is the most common chemical sample modification performed in IC. Usually, it is not possible to just add a base or an acid in order to alter the pH, as doing so would introduce a contaminant cation or anion. [47] These contaminant ions may severely interfere with other analyte ions to be quantified [17]. Highly alkaline samples are especially challenging for anion chromatography as peaks suffer from deformation, baseline disturbances, system peaks appear and column lifetime is reduced [20]. With suppressed conductivity detection, samples showing a NaOH concentration in the range of 0.3 mol/L are suitable for direct injection of the sample into the IC system [47]. Higher concentration may require one of the following pretreatment methods.

Strong cation-exchange resins in the hydrogen form can be added to an alkaline sample to lower the pH. However, ion-exchange resins have some drawbacks: large sample volumes are necessary for this procedure, the resin must be thoroughly cleaned to prevent contamination of the samples by ions leaching from the resin, the sample volume can change due to uptake or release of solvent from the resin and sample components can be adsorbed by the resin material and are consequently lost for the analysis. [47]

Donnan dialysis is another sample preparation method in such cases. This technique uses a cation-exchange membrane to replace sodium ions of the sample with hydronium ions from an acidic donor solution. The donor solution and the sample are separated by the cation-exchange membrane. Samples are introduced to the dialysis apparatus by a syringe or a pump. The effluent of the dialysis can be injected into the IC apparatus. Electrodialytic neutralization could be applied to highly alkaline or highly acidic samples. Concentrations of up to 1 mol/L NaOH or acid solutions could be neutralized within 10 min. [20]

If low concentrated analytes of interest have to be separated from their interfering matrix (e.g. because of its high ionic strength), solid phase extraction is often the method of choice [17,20,24]. Reducing the sample load on the column by dilution or the usage of a smaller sample loop does not provide a solution to this problem [20,24]

Solid phase extraction (SPE) is performed by passing the sample through a cartridge filled with a sorbent material, that either retains the analyte ions or the matrix ions [17]. In the first case the matrix ions are discarded with the effluent and the analyte ions have to be desorbed from the resin prior to analysis. In the second case the effluent of the cartridge can be used for IC detection. [20] Multiple ready-to-use cartridges are available on the market. Passing the sample through such a cartridge can be done manually, semi-automatically or fully automatically. [17] Recently, besides packed bed columns also disk shaped SPE columns, which do not show channeling effects, are commercially available. Additionally, they have a large flow area, bed masses as well as their void volume (i.e. 10 µL to 50 µL) are low. Generally speaking, SPE can be easily automated, it is less prone to contamination than other techniques and high enrichment factors can be achieved. For the selec-

tive removal of chloride Dionex OnGuard Ag cartridges are suitable. Here, chloride is trapped on an ion-exchange resin in the silver form. A major disadvantage of this material is that silver can leach from the column which can deteriorate the analytical column. To overcome this, a metal trap column can be used. [20]

2.2 Electrodialysis

Electrodialysis is a technology that enables the separation of ionic species from aqueous solutions in a direct current field, using clever arrangement of ion-exchange membranes [13, 48–56]. Cations migrate towards the cathode and anions migrate towards the anode [48,49,51,55,56]. The migration rate of the ions can be controlled by the current density [51]. Electrodes, placed in an electrolyte solution, transfer the current [48, 51, 53]. They are usually inert and plate-shaped. Gas bubbles form at the electrode-solvent interface. In aqueous systems for example H_2 and O_2 gas arise from water electrolysis. [51] There are several possible electrodialysis configurations. Here, mainly bipolar electrodialysis will be discussed as this technique will be used in the following experiments.

In bipolar electrodialysis cation-exchange membranes (CEM), anion-exchange membranes (AEM) and bipolar membranes (BPM) are alternately arranged in a direct current field [13, 51, 55, 57]. Ion-exchange membranes are made from polymeric materials carrying ionizable groups on their surface [48]. CEM mainly carry SO_3^-, COO^-, PO_3^{2-} or PO_3H^- groups, and AEM mainly carry alkyl ammonium groups like NR_3^+, NHR_2^{2+} or NH_2R^+ [48, 56, 57]. CEM and AEM prevent the transport of co ions, anions and cations, respectively [13, 48, 49, 51, 56]. The exchange of cations and anions between the membranes and the surrounding liquid is diffusion controlled. Bipolar membranes are composed of an anion-exchange layer, a cation-exchange layer, and a hydrophilic interface at their junction. In presence of a direct current, water molecules migrate into the hydrophilic layer, where they are split into H^+ and OH^-. [13,48,51,57] The energy required for the water dissociation is calculated with the Nernst equation (formula 2.14). ΔG is the Gibbs free energy, F is the Faraday constant, R is the gas constant, T is the temperature and ΔpH and $\Delta\phi$ are the pH difference and the potential difference between the two solutions separated by the bipolar membrane. [57] Ion-exchange membranes need to have high permselectivity, low electrical resistance, good mechanical resistance, high form stability as well as high chemical and thermal stability. [57]

$$\Delta G = F\,\Delta\phi = 2.3\,R\,T\Delta pH \tag{2.14}$$

2.2.1 Transport Phenomena in ED

Basically there are two major transport processes which are relevant for electrodialysis. On the one hand diffusive transport along a concentration gradient and on the other hand migration due to a potential difference take place. These two

processes can be considered independent from each other and are expressed by the Nernst-Planck equation: [56]

$$\dot{n}_j = -D_j \frac{\partial c_j}{\partial x} - z_j c_j D_j \frac{F}{R T} \frac{\partial \phi}{\partial x} \tag{2.15}$$

This equation demonstrates that the molar flow density of an ion $\dot{n}_j$ equals the sum of the diffusive and migrative molar flow densities, where the direction of transport is defined by the sign of the referring gradients $\partial c_j/\partial x$ and $\partial \phi/\partial x$ as well as the charge number z_j of the component j. D_j is the diffusion coefficient of j.

Mass transfer by migration is larger inside the membrane than in the diluate, as it is proportional to the concentration c_j. On the surface of the membrane facing the diluate, ion depletion takes place, whereas on the membrane side facing the concentrate, accumulation of ionic species occurs. If the current density is further increased the ion concentration at the membrane surface can approach 0. This can cause water dissociation and the limiting current density is reached. As calculation of the limiting current density is not or only hardly possible in reality it is usually determined experimentally. [58, 59]

Water transport across the membranes causes convective transport of ions. Pressure gradient, dragging effects of migrating ions, transport of water as part of the hydration shell of ions and osmosis are mechanisms that influence its extent. The pressure gradient between the different compartments should be as small as possible. Ideally, no pressure difference is present. The dragging effect of migrating ions moves the liquid trapped inside the pores. This process is also known as electroosmosis. [58]

Ions in a watery liquid are surrounded by a hydration shell. Depending on the size and charge of the ion the hydration shell contains four or more water molecules. These water molecules are transported in the same direction as their referring ions. Furthermore, water is transported to the concentrate compartment due to osmosis. [58]

2.2.2 Fouling of Ion-Exchange Membranes

From a separation technology point of view the most challenging component in black liquor is lignin [4, 6]. Solubility of lignin depends mainly on the temperature, the pH value and the ionic strength. It was shown that lignin precipitation starts at a pH value of 11.5. [5] Lignin shows a colloidal structure when precipitated. This property makes it difficult to separate from liquids. Membranes, chromatographic support materials and ion-exchange membranes were reported to be prone to fouling by lignin adsorption [4, 6]. Especially anion-exchange materials were found to be easily fouled by organic matter [6, 60].

Fouling is an unfavorable phenomenon that all membrane separation processes suffer from [56, 57]. Fouling can either be caused by the attachment of a substance or a living organism to the membrane surface. Colloidal fouling, organic fouling and biofouling are the three types of fouling affecting ion-exchange membranes. [56]

Suspended solids that carry either positive or negative charges, e.g. polyelectrolytes like lignin [53], humic acids or surfactants, are often identified as the source of fouling [57]. Apart from fouling, membrane scaling can happen when a dissolved species precipitates onto the membrane surface [56].

The applied current determines the amount of ions being transported through the membranes. If the current is increased, more ions are transported. At the same time charged foulants move towards their referring electrode. However, due to the permselectivity of the membranes they are rejected and deposited on the membrane surface. As the amount of foulants on the surface of the membrane increases, the formed fouling gel layer becomes thicker and more compact. Once a compact gel layer is present, ions cannot move freely anymore. [50] This results in increased resistance [50,57]. The fouling gel layer can become an additional electric resistance in determining the current density at a given cell voltage [50]. Therefore, fouling in electrodialytic applications causes increased levels of energy consumption resulting from significant efficiency drops [60].

Mishra and Bhattacharyya observed lignin fouling on anion-exchange membranes during electrodialytic treatment of spent liquor. They observed that voltage requirements were high and the rate of electrodialyis decreased at longer residence time because of fouling. They explained lignin precipitation by the following phenomena: On the one hand lignin is present in black liquor as the sodium salt of phenol or sulfonic acid. It dissociates and is attracted to the anode. As it cannot pass the membrane due to its size, it forms a layer on the membrane surface. On the other hand the pH value of spent liquor decreases during the experiment, and therefore, Kraft lignin starts to precipitate. [14]

Fouling of anion-exchange membranes was investigated using negatively charged organic foulants like humate, bovine serum albumin and sodium dodecylbenzenesulfonate. Lee et al. argue that organic foulants are mostly negatively charged molecules having a high molecular weight. Such molecules accumulate on the membrane surface and foul it due to deposition and/or adsorption. Fouling increases the resistance, as it slows the transport rate through the inner structure of the AEM. [61]

Detailed information of the fouling behavior of different CEMs and BPMs during electrodialytic treatment of Kraft black liquor was reported by Haddad et al. Colloidal fouling behavior having negative effects on the membranes' performance was observed. The thickness of fouled bipolar membranes was found to be four times the thickness of a fresh BPM. The thickness of the cation-exchange membranes increased between 8 % and 33 %. After electrodialysis the side of the ion-exchange membranes exposed to black liquor was contaminated with foulants. Using energy dispersive X-ray analysis it was found that the deposit layer consisted mainly of carbon, oxygen and small fractions of sodium and sulfur. The determined O/C ratio of the foulants is in good agreement with the O/C ratio of Kraft lignin. Cleaning cycles were required and caustic soda as well as fresh, diluted black liquor were tested as cleaning solutions. With caustic soda no contamination was detected on the ion-exchange membranes after the cleaning step. For two types of cation-exchange

membranes (CMB and Nafion 324) the initial properties could be reestablished after the cleaning procedure. Lignin precipitation and the chemical cleaning procedure did not change the electrical resistance of the cleaned CBM and Nafion 324 membranes. However, the electrical resistance of the cleaned FKB and CM(H)-PES membranes were increased by 10 %. This was independent of the type of cleaning solution and may be attributed to the presence of small amounts of foulants (lignin particles) on the surface or inside these membranes. Another possible reason is the appearance of minor membrane damages during the electrodialysis experiment or the cleaning steps. [53]

Apart from lignin fouling also peptide and protein fouling were observed on anion-exchange membranes. Protein foulants form a gel layer on the membrane surface. [56, 61]

The second major problem of membrane processes is concentration polarization. In electrodialysis concentration polarization causes the accumulation of ions on the membrane surface facing the concentrate compartment. If the concentrations exceed the solubility limit, salt precipitation occurs. Simultaneously, on the diluate side of the membrane ion depletion happens. If the concentration approaches 0, the limiting current density is reached. This means that a further voltage increase would not result in a current increase. [57]

Salts present in the feed solution were reported to change the counter-ion concentration within the membranes. This affects the performance of the membranes. Calcium present in the feed solution can replace counter ions of the membranes and thereby change their electrical conductivity. Calcium salts precipitate with increasing temperature. [56] This might be a problem in electrodialysis as the temperature of the liquid streams increases due to friction [49].

Cleaning procedures helped to remove fouling layers. $CaCO_3$ scaling was removed by a HCl (pH 2) treatment, which converts the salt to CO_2. [62] Other authors claimed that performing the electrodialytic treatment of black liquor below $20\,mA/cm^2$ prevents the precipitation and polarization due to lignin fouling [63]. In electrodialysis foulants might also be removed by reversing the polarity of the applied potential. This causes the removal of charged species from the membrane. [57] Another possibility to avoid membrane fouling caused by lignin is to remove lignin prior to electrodialysis. Multiple authors reported on the successful separation of lignin and hemicelluloses by ultra- or nanofiltration. [1, 4, 64, 65]

2.2.3 Electrodialysis in Pulp and Paper Industry

Batch as well as continuous electrodialysis of black liquor was preformed by Mishra and Bhattacharya. Their goal was to recover soda from the spent pulping liquor. [14, 63] Similar experiments were carried out by Radhamohan and Basu [60].

Partial recovery of sodium as NaOH and free aliphatic carboxylic acids from hardwood black liquor was investigated by Kumar and Alen. In their first approach they used carbonated black liquor as feed for the electrodialysis. Free acids and NaOH were recoverd. For the second approach the carbonated black liquor was

further acidified with H_2SO_4. The resulting Na_2SO_4 was precipitated with methanol and used as alternative feed for the electrodialysis with the aim to produce H_2SO_4 and NaOH. All experiments were performed in a batch electrodialysis apparatus in bipolar configuration at constant voltage of 20 V. [13]

Microfiltration combined with electrodialysis was carried out by Nataraj et al. to remove colors and contaminants from wastewater of the paper industry. Microdialysis had the purpose to prefilter the wastewater. After both unit operations, more than 90 % of the original wastewater could be reused. [62]

A patent of Rowe et al. describes a process to separate aliphatic organic acids from Kraft black liquor. They subjected the liquor to ultrafiltration and treated the permeate by electrodialysis. The concentrate of the electrodialysis then contained Na-lignin and aliphatic organic acids. Further acidification to about pH 4 to 5 was performed. H-lignin was separated. Several further steps follow until organic acids could be recovered. [12]

3 Materials and Methods

3.1 Ion Chromatography

A Dionex Integrion ion chromatography system is used, combined with a Dionex AS-DV autosampling device. The eluent is generated with potassium hydroxide from a Dionex EGC 500 KOH eluent generator cartridge and high purity water ($\rho > 17.5\,\mathrm{M\Omega\,cm}$, TOC $< 40\,\mathrm{ppb}$) from the ultrapure water system available at the Institute of Chemical Engineering and Environmental Technology. A Dionex CR-ATC 600 continuously regenerated anion trap column is installed.

For the HPAEC-PAD application a Dionex Integrion electrochemical detector is combined with a Thermo Scientific electrochemical cell. A Thermo Scientific ED gold electrode (solid electrode) and a Dionex pH-Ag/AgCl electrode are mounted to the electrochemical cell. The gold electrode is used as the working electrode and the Ag/AgCl electrode is used as the reference electrode. In case of routine measurements, solid gold electrodes are to be preferred. In case of troubleshooting Thermo Scientific disposable gold electrodes (carbohydrate certified) are used.

In the HPAEC-sCD a Thermo Scientific conductivity cell is installed, with a Dionex ASRS 300 2 mm electrolytically self-regenerating suppressor mounted onto the conductivity cell.

The separation of carbohydrates is performed on a Dionex CarboPac PA20 ($3 \times 150\,\mathrm{mm}$) analytical column combined with a Dionex CarboPac PA20 ($3 \times 30\,\mathrm{mm}$) guard column. For the separation of organic acid anions and inorganic anions a Dionex IonPac AS11-HC ($2 \times 250\,\mathrm{mm}$) analytical column is used. A Dionex IonPac AG11-HC ($2 \times 50\,\mathrm{mm}$) guard column is installed prior to the AS11-HC analytical column.

Chromeleon 7, a chromatography software of Thermo Scientific was used for evaluation of both, HPAEC-sCD and HPAEC-PAD.

3.1.1 Chemicals, Equipment and Standard Solutions

Aqueous standard solutions of acetate, carbonate, formate, glycolate, lactate, oxalate and succinate were purchased from Sigma-Aldrich. Each solution has a concentration of 1 g/L of the referring anion. For detailed information consult the certificates of analysis in the appendix. Phosphate (KH_2PO_4 in water), chloride (NaCl in water) and sulfate standard solutions (Na_2SO_4 in water) were obtained from Merck. The exact concentrations of phosphate, chloride and sulfate are $1001 \pm 2\,\mathrm{mg/mL}$, $1001 \pm 2\,\mathrm{mg/mL}$ and $998 \pm 2\,\mathrm{mg/mL}$. A Titrisol® 1 mol/L KOH cartridge was purchased from Merck. Concentrated HCl (37 %, $\rho = 1.19\,\mathrm{g/cm^3}$,

MM = 36.46 g/mol) was purchased from Roth. Dionex OnGuard II Ag 1 cm^3 cartridges were obtained from ThermoFisher Austria.

3.1.2 Standard Preparation and Calibration

All standard solutions were kept at room temperature the night before the standard solution was prepared in order to get the standard solutions from refrigerator temperature to room temperature. According to the information sheets of the standard solutions, each standard was shaken thoroughly before usage.

A mix standard was prepared from nine single standard solutions such that the concentration of each anion in the mix is 100 mg/L. The mix standard contained acetate, carbonate, chloride, glycolate, lactate, oxalate, phosphate, succinate and sulfate. The 100 mg/L formate standard must be prepared separately as formate is present as its calcium salt, which forms insoluble calcium oxalate in the mix standard. All further dilutions were prepared from the 100 mg/L standard solutions by volumetric dilution. Dilutions were exclusively prepared in ultrapure water, using tubes made from plastic. Glass ware was always avoided.

As lactate, acetate and glycolate elute very early and peaks are close together these components were calibrated in the range of 1 mg/L to 15 mg/L. Calibration standards with a concentration of 1 mg/L, 3 mg/L, 5 mg/L, 7 mg/L, 10 mg/L and 15 mg/L were prepared in duplicates.

Carbonate, chloride, formate, oxalate, phosphate, succinate and sulfate were calibrated from 1 mg/L to 50 mg/L. Calibration standards with a concentration of 1 mg/L, 3 mg/L, 5 mg/L, 7 mg/L, 10 mg/L, 15 mg/L, 25 mg/L and 50 mg/L were prepared in duplicates.

The *Chromeleon 7* function `Processing and Calibration` was used to create a linear calibration curve. The CobraWizard algorithm was used for peak detection and identification. Manual corrections were performed if necessary.

3.1.3 OnGuard II Ag Cartridge Recovery Experiment

The Dionex OnGuard II Ag 1 cm^3 cartridge was prepared for operation following the instruction in the manual [66]. The cartridge was flushed with 10 mL of deionized water using a 5 mL luer-lock plastic syringe. This syringe type provides cartridge back pressure in the correct range. The maximum flow rate of 2 mL/min was monitored by a stopwatch.

To derive a correlation for the recovery of different organic acid anions and the removal of chloride, four dilutions of the mix standard and the formate standard described above were treated with the OnGuard II Ag cartridge. The concentrations of the four dilutions were 1 mg/L, 5 mg/L, 10 mg/L and 50 mg/L. 5 mL of each dilution were passed through the OnGuard II Ag cartridge, starting with the highest dilution to prevent carryover. The luer-lock syringe used was combined with a 0.45 µm syringe filter to trap particles eluted from the OnGuard cartridge. The first 3 mL of each sample have to be discarded. The remaining 2 mL can be used for IC

analysis. An OnGuard treated sample was compared to the referring concentration of an untreated sample and the recovery percentage was determined for each anion.

3.1.4 Sample Preparation for HPAEC-sCD Analysis

The properties of the solutions present in the acid, base and salt compartment of the electrodialysis apparatus are diverse. Appropriate sample preparation procedures prior to IC analysis are therefore essential.

Samples withdrawn from the base compartment do not have to be diluted as the concentration of the organic and inorganic anions is very low. These samples are passed through a 0.45 µm syringe filter to remove particulate matter.

In case of an experiment with black liquor model solution, the acid compartment contains 10 mmol/L HCl to provide a conductive environment. Additionally, most anions are present in their free acid form at such a low pH value. 10 mmol/L HCl refers to a concentration of 364.6 mg/L, which is very high compared to the expected amounts of organic acid anions. Therefore treatment with Dionex OnGuard II Ag cartridges was necessary. To be able to use the same cartridge for all acid samples of an experiment, appropriate pre-dilutions were prepared. Early samples were diluted by a factor of 2 and later ones by a factor of 10. All samples were diluted in 5 mL or 10 mL volumetric flasks. The OnGuard II Ag cartridge was prepared as described above. Pre-diluted samples were passed through the cartridge at a flow rate of approximately 2 mL/min. To prevent carryover, the samples were treated in ascending order of their organic acid concentration. 5 mL luer-lock plastic syringes combined with 0.45 µm syringe filters were used to pass the samples through the cartridge. The first 3 mL of each sample were discarded and the remaining 2 mL were collected for further treatment. To convert the free organic acids to their potassium salts 10 µL of 1 mol/L KOH are added per 900 µL of Ag cartridge treated sample. The pH value was checked by a universal pH indicator paper and was between 10 and 12 for all samples. If necessary, samples were further diluted in ultrapure water to an overall dilution factor of 100.

Salt compartment samples of an experiment with black liquor model solution are passed through a 0.45 µm syringe filter. Samples were diluted in ultrapure water to a maximum dilution factor of 1000. Several intermediate dilution steps of factor 10 were performed in such cases.

In case of an experiment with diluted black liquor the acid and base compartment samples were passed through a 0.45 µm syringe filter. Acid samples were diluted appropriately in ultrapure water. Sample preparation for aliquots withdrawn from the salt compartment was complex. At first, lignin was removed by precipitation with HCl. 900 µL of a diluted black liquor sample were mixed with 300 µL of 1 mol/L HCl in an Eppendorf tube. The samples were centrifuged using a Haereus Sepatech Biofuge 17 RS centrifuge (Rotor 1387) for 10 min at room temperature and 10 000 rpm speed. The pH of the supernatant was checked with an pH indicator paper for the acidic range and showed a value between 0.5 and 1 for all samples. The clear and yellowish supernatant was diluted by a factor of 40 in a 20 mL

volumetric flask using ultrapure water. To remove chloride, samples were treated by an OnGuard II Ag cartridge. To prevent carryover, samples were passed trough the cartridge in ascending order of their organic acid concentration. 5 mL luer-lock plastic syringes combined with 0.45 µm syringe filters were used for the procedure. The first 3 mL of each sample were discarded and the remaining 2 mL were collected for further treatment. To convert the free organic acids to their potassium salts, 10 µL of 1 mol/L KOH were added per 900 µL of Ag cartridge treated sample. The pH value was checked by a universal pH indicator paper and was between 10 and 12 for all samples. If necessary samples were further diluted in ultrapure water to an overall dilution factor of 213.

All samples are measured in duplicates. Additionally, before starting a measurement sequence, after every tenth sample and after terminating a measurement sequence, ultrapure water and a check standard were measured. The check standard contains 10 mg/L acetate, carbonate, chloride, glycolate, lactate, oxalate, phosphate, succinate and sulfate and is always prepared from the same 100 mg/L stock solution.

3.2 Electrodialysis

A laboratory scale electrodialysis apparatus purchased from Hescon GmbH was used for all experiments. Cation-exchange membranes of type fumasep® FKB-PK-130, anion-exchange membranes of type fumasep® FAB-PK-130 and bipolar membranes of type fumasep® FBM-PK were obtained from Fumatech BWT GmbH. Polymeric spacer sheets were supplied with the electrodialysis apparatus. Two end spacers separate the electrodes from the first cation-exchange membrane. The intermediate spacers separate all other compartments and simultaneously protect the membranes from mechanical damage. The electrodialysis apparatus is combined with an EA Elektro-Automatik EA-PS 3032-10 B laboratory power supply. The power supply unit is remote controlled by a UTA12 analog-to-digital converter. The necessary software for the UTA12 works under Microsoft Windows XP or higher.

3.2.1 Chemicals

Sodium hydroxide pellets and sodium azide with a purity of 99 % were purchased from Merck. Sodium chloride with a purity of 100 % was obtained from Roth. Concentrated HCl (37 %, $\rho = 1.19\,\mathrm{g/cm^3}$, MM = 36.46 g/mol), pure acetic acid (100 %, $\rho = 1.05\,\mathrm{g/cm^3}$, MM = 60.05 g/mol) and lactic acid (80 %, $\rho = 1.2\,\mathrm{g/cm^3}$, MM = 90.1 g/mol) were purchased from Roth. Sodium formate with a purity of 100 % was obtained from Merck.

3.2.2 Start-Up of the Electrodialysis Apparatus

Before the first experiment can be started, the anion-exchange, cation-exchange and bipolar membranes have to be stacked correctly. This has to be performed on

a clean and dust free surface to prevent membrane damage.

The membrane stack is separated from the electrodes by two endspacers (dark blue frame). If stacking is started from the endspacer at the cathode, a cation-exchange membrane has to be placed on top of the endspacer, followed by a spacer (light blue frame). Now the first cell triple can be started.

A cell triple consists of a cation-exchange membrane, an anion-exchange membrane and a bipolar membrane. In figure 3.1 one cell triple is indicated by a dashed frame. The bipolar membrane has to be placed such that the side of the membrane facing the cathode shows the small hole on the lower left side and the cut off corner on the lower right side (compare figure 3.1). All membranes need to be separated by spacers as the orientation of the spacers determines the flow path of the liquid. Five cell triples are stacked according to the scheme shown in figure 3.1. On top of the last cell triple a cation-exchange membrane has to be placed, followed by an end spacer. This end spacer separates the membrane from the anode.

As soon as stacking is terminated the membrane stack has to be placed on top of one electrode. The orientation of the spacers has to be kept in mind to be able to connect the stack with the ports of referring pipes and compartments. If this is done the second electrode can be placed on top of the membrane stack and the whole stack can be closed with the threaded bars and screw-nuts. The stack has to be closed tightly and uniformly. A tightening torque of 15 N m is recommended.

Unused membranes are stored in 1.5 wt% NaCl solution with 100 ppm NaN_3 to prevent microbial growth. Sealed plastic bags are used for storage. The bags containing the membranes are stored at room temperature and protected from light.

Before turning on the electrodialysis apparatus it must be ensured that only the fuse of the power socket and the fuses of the pumps in use are switched on. Now the power supply cable of the apparatus can be plugged into a wall socket. The toggle switch is still off (position 0).

Compartments are filled with liquid. All valves have to be closed when doing so. To vent the pumps the ball valves (KH102, KH302, KH402 and KH502) have to be opened, while the membrane valves (MV101, MV301, MV401 and MV501) have to stay closed. Now, the toggle switch can be set to position 1 to switch on the pumps. Pumps are vented for 15 s. If pumps make unsteady noise the filling level of the referring compartment is too low and air is sucked in by the pump. In this case the toggle switch has to be set to position 0 and more liquid has to be filled into the respective compartment. Pump venting has to be repeated.

If the pumps are completely vented, the membrane valves (MV101, MV301, MV401 and MV501) can be slightly opened. Membranes valves should be opened simultaneously and evenly. After closing the ball valves membrane valves can be further opened until the desired pressure is adjusted at each compartment. Membrane valve MV101 referring to the electrolyte circuit is opened completely. The default pressure value for acid, base and salt compartment is 0.3 bar and the pressure setting of the electrolyte circuit at fully opened membrane valve is 0.15 bar. Pressure in the electrolyte circuit is always lower than in the remaining circuits. After all pressure values are constant the experiment can be started by switching

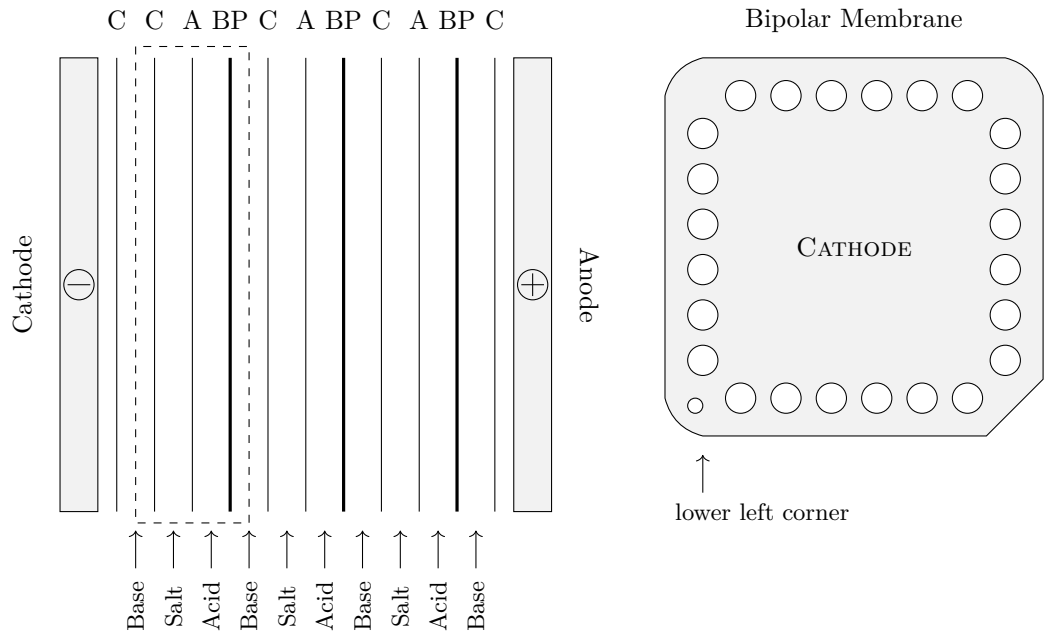

Figure 3.1: Scheme of the membrane stack. C, A and BP indicate the cation and anion-exchange membranes, and the bipolar membranes. Bipolar membranes are correctly oriented if the word cathode on one side of the membrane faces the cathode.

on the power supply of the membrane stack.

During electrodialytic treatment oxyhydrogen gas is produced due to the electrodes being directly contacted with the electrolyte. If the power supply is operated at 10 V and 100 % efficiency for this reaction is expected, approximately 4200 mL of hydrogen gas are produced per hour. To keep the hydrogen concentration below the lower explosion limit of 4 %, it is necessary to constantly aerate the electrolyte compartment. This is realized by leading pressurized air into the electrolyte compartment. The electrolyte compartment is kept open to allow gas exchange. As the pressurized air line transports some oil it is necessary to clean the air using a gas washing bottle filled with deionized water, to avoid contamination of the electrolyte.

All experiments are performed in the bipolar electrodialysis configuration. The maximum operation temperature for this configuration is 39 °C and the maximum current density is 80 mA/cm^2. As the effective membrane area is 100 cm^2 the maximum current is 8 A, the maximum voltage is 20 V.

The experiments described in the following sections were conducted at constant voltage of 10 V. The produced current is recorded by the EA-PS 3032-10B laboratory power supply. Additionally, the electric power of the electrodialysis apparatus is calculated for each experiment according to:

$$P(t) = I(t) \times V(t) \tag{3.1}$$

3.2.3 Electrodialytic Treatment of Black Liquor Model Solution

In all electrodialysis experiments 1 mol/L NaOH was used as electrolyte. The NaOH solution was prepared from solid NaOH pellets dissolved in deionized water. As the volume of the electrolyte compartment is smaller than that of the other compartments, 1 L of electrolyte was sufficient.

3 L of 10 mmol/L NaOH solution were used as a starting solution in the base compartment. This solution provides an appropriately high conductivity in the beginning of the experiment. Additionally, NaOH is supposed to be concentrated in the base compartment during the experiment. Therefore, diluted NaOH does not introduce other components into the compartment.

3 L of 10 mmol/L HCl were used as a starting solution in the acid compartment to increase the conductivity in the beginning of the experiment. Chloride introduced in this way is removed by treatment with OnGuard II Ag cartridges prior to IC measurements.

The salt compartment of the electrodialysis apparatus was filled with 3 L of black liquor model solution. This solution was prepared from a 4 mol/L acetic acid stock solution, a 2 mol/L lactic acid stock solution and a 100 g/L sodium formate stock solution. The stock solutions were diluted with deionized water such that the black liquor model solution contained roughly 5 g/L acetate, 5 g/L lactate and 3 g/L formate. The pH was adjusted using NaOH pellets until a pH value of 13 was reached. The pH was checked with a pH indicator paper for the alkaline range. The pH values of the acid, base and salt compartment were determined using a WTW MultiLine P4 Universal Meter. To determine the pH values of the acid compartment the pH meter was calibrated between pH 4 and 7. To determine the pH values of the salt and the base compartment it was calibrated between pH 7 and 10. The conductivity was determined using a WTW LF 521 conductivity meter combined with a WTW LTA 1 conductivity electrode. All samples were measured at room temperature. The exact acid concentrations were determined by IC analysis before the electrodialysis experiment was started. During the whole experiment samples for IC analysis were withdrawn from the acid, base and salt compartment. If samples were not analyzed immediately they were kept in the refrigerator until measurement.

After an experiment with black liquor model solution is finished, the whole electrodialysis apparatus is flushed with deionized water. The deionized water is removed from the system and the system is flushed again with storage solution to prevent the membranes from drying out. For overnight storage it is sufficient to use a 1.5 wt% NaCl solution. For longer storage periods a 1.5 wt% NaCl solution with 100 ppm NaN_3 is used to prevent microbial growth. Figure 3.2 shows the transport principle of ions in a bipolar electrodialysis apparatus.

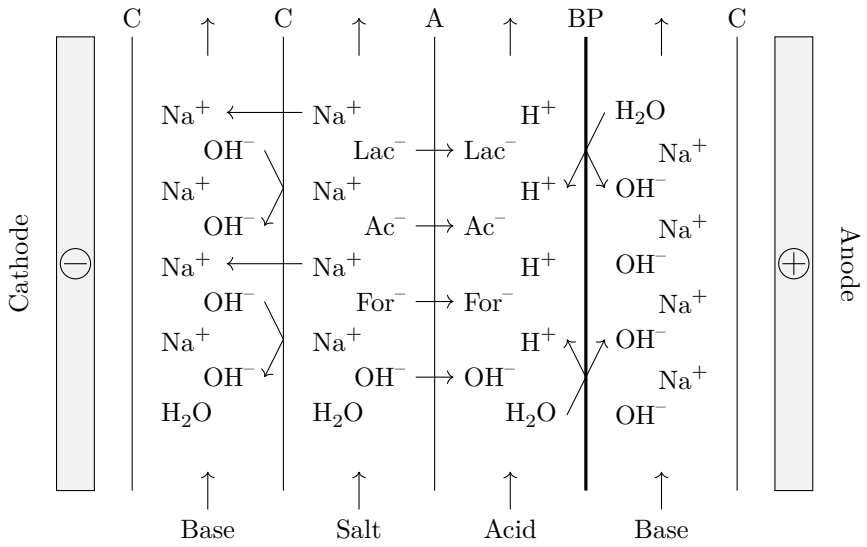

Figure 3.2: Transport principle of ions within bipolar electrodialysis. C, A and BP indicate the cation-exchange, anion-exchange, and bipolar membranes. Lac, Ac and For stand for lactate, acetate and formate.

3.2.4 Electrodialytic Treatment of Diluted Black Liquor

Similar to the experiments with black liquor model solution, 1 mol/L NaOH was used as electrolyte. The base compartment was filled with 10 mmol/L NaOH. To reduce the formation of toxic H_2S gas, the acid compartment was filled with 10 mmol/L NaOH solution too. If necessary, 10 mL of 1 mol/L NaOH were added to the acid compartment to keep the H_2S concentration below a critical value.

Black liquor from a local paper mill with a total dry substance content (TDS) of 41.6 % was used for both experiments. To reduce the TDS content to 5 % dilution with deionized water was performed. This refers to a dilution factor of 8.3. 3 L of diluted black liquor were used for each experiment.

Before and during the experiment, samples of each compartment were withdrawn. The pH value was measured with a WTW MultiLine P4 Universal Meter. The conductivity was determined using a WTW LF 521 conductivity meter combined with a WTW LTA 1 conductivity electrode. All samples were measured at room temperature. The concentrations of organic acid anions were determined by IC analysis. If samples were not analyzed immediately, they were kept in the refrigerator until measurement.

After black liquor treatment was finished and all compartments were completely emptied, the electrodialysis apparatus was flushed with 100 mmol/L NaOH twice to remove precipitated lignin. Afterwards the system was flushed with deionized water and storage solution as mentioned earlier.

4 Commissioning of the HPIC System

The Dionex Integrion HPIC system present at the Institute of Chemical Engineering and Environmental Technology can be used in two different set-ups. On the one hand it is suitable for the separation and detection of inorganic and organic anions using suppressed conductivity detection combined with a column suitable for anion separation, e.g. IonPac AS11-HC. On the other hand sugars and sugar alcohols can be separated and detected using an amperometric detector combined with a column suitable for sugar separation, e.g. CarboPac PA20. In this chapter the main focus is set upon switching between the two different detection systems and their referring columns. The most important steps to start everyday operation are summed up in table 4.1. At the end of this chapter some examples of troubles emerged during commissioning phase of the HPIC system and solutions are shown.

4.1 Installation of HPAEC-sCD with IonPac AS11-HC

Before starting with the installation of the conductivity detector make sure that the HPIC apparatus is switched off. Open the compartment door on the right side at the bottom of the HPIC instrument. Put the conductivity cell into the blank space of this compartment. This is the space where the electrochemical cell is located, if the amperometric detector was installed before. Be careful when plugging the conductivity cell into the plug. Close the two cross-headed screws. Mount the suppressor on top of the conductivity cell. Connect the capillary leaving the analytical column with the suppressor using the "Eluent In" port. Connect the "Regen Out" port of the suppressor with the tube leading to the "Regen In" port of the CR-ATC. The CR-ATC removes trace level anionic contaminants from the ultrapure water used as eluent. In figure 4.1 b) the correctly plumbed conductivity detector can be seen. Figure 4.1 a) shows the entire HPIC system in the HPAEC-sCD configuration. After plugging the black cable into the referring plug, it can be proceeded with steps 1 to 4 of table 4.1.

To implement the conductivity detector in the software press `Configure Instrument` in the *Chromeleon Service Manager*. Select `Integrion HPIC System` under `IC` in the directory tree. Make sure that the check boxes `Suppressor`, `CR-TC` and `Eluent Generator` in the `Electrolytics` tab, as well as the check box `CDet` in the `Detector` tab are ticked. Save the instrument configuration under `File/Save Installation`. Close *Chromeleon Service Manager*, open *Chromeleon 7* and connect the HPIC device and the autosampler (compare step 6 of table 4.1). Make a consumables inventory by selecting `Inventory` under `Consumables` in the *Chromeleon Console*. Here, the guard and the analytical column, as well as the

Figure 4.1: a) The Dionex Integrion HPIC system in HPAEC-sCD configuration. b) The correctly plumbed suppressed conductivity detector.

eluent generator cartridge and the CR-ATC should be listed. If so make sure that all their check boxes are ticked and close the window. If any of them is not represented, make sure that all compartment doors are closed (RFID tags are might not be recognized if doors are open) and press `Rescan`. If all expected consumables are found, press `Approve` and close the window as soon as approval is finished. Proceed with step 7 of table 4.1.

If a suppressor is installed for the first time, read the referring manual first as instructions deviate from the above ones. In case 2 mm columns are used, it is tremendously important to keep the system void volume small. For optimum performance, it is recommended to use only red tubing for all connections between the injection valve and the detector. Generally, all tubes between the injection valve and the detector should be kept as long as necessary but as short as possible. If a capillary has to be cut, always use the capillary cutter and move it in circular motion around the capillary until it breaks. This avoids damage of the inner diameter of the capillary. Furthermore, on a 2 mm system the sample loop used should have a

volume of 2 µL to 15 µL to avoid overloading of the column.

Before removing the conductivity detector, flush the suppressor thoroughly with ultrapure water (at least 1 h at standard flow rate of 0.38 mL/min). Eventually, bypass the guard and analytical columns for this step. Switch off the HPIC apparatus. Unplug the connection between the analytical column and the suppressor as well as the connection between the CR-ATC and the suppressor. Seal the suppressor and all open capillaries and tubes with dummy plugs. Remove the suppressor from the conductivity cell. Open the two cross-headed screws and unplug the conductivity cell carefully from its plug.

To install an IonPac AG11-HC 2×50 mm guard column or AS11-HC 2×250 mm analytical column for the first time or to reinstall them after long-term storage, both of them have to be flushed separately with 20 mmol/L KOH. This means that the guard column is connected to the 6-way valve of the HPIC system and the concentration of the eluent generator is set to 20 mmol/L. Use the standard flow rate of 0.38 mL/min and flush the guard column for at least 30 min. Eluent leaving the guard column is collected in a beaker glass. During this procedure it has to be ensured that the suppressor and the CR-ATC are switched off to avoid damage. After flushing of the guard column is finished, the analytical column can be connected to the guard column. Keep the direction of flow, which is indicated on both columns, in mind. The analytical column is flushed for at least 60 min using the same settings as before. Eluent leaving the analytical column is collected in a beaker glass. After flushing is finished the analytical column can be connected to the suppressor. Proceed with step 12 of table 4.1. Under operation conditions the maximum flow rate for the IonPac AG11-HC guard column and the AS11-HC analytical column is 0.75 mL/min. The typical system pressure is 1950 psi. If the system pressure rises above 2250 psi system contamination by particulate matter has to be assumed.

For short-term storage (weeks) the columns are flushed with 20 mmol/L KOH and tightly capped using black dummy plugs. For long-term storage (one month or more) it is recommended to use 100 mmol/L sodium borate solution. Avoid contact of sodium borate and the suppressor.

Further information on the devices being part of the HPIC system, installation and cleaning procedures can be found in their respective manuals. Information and examples concerning separation of various ions and a comprehensive trouble shooting guide are included in the column manuals [67].

4.2 Installation of HPAEC-PAD with CarboPac PA20

Before starting with the installation of the electrochemical detector, make sure that the HPIC apparatus is switched off. Open the detector compartment door on the right side at the bottom of the HPIC instrument. Plug the electrochemical cell into the blank space of this compartment. If the conductivity detector was installed before, this is the space where the conductivity cell is located. Be careful when

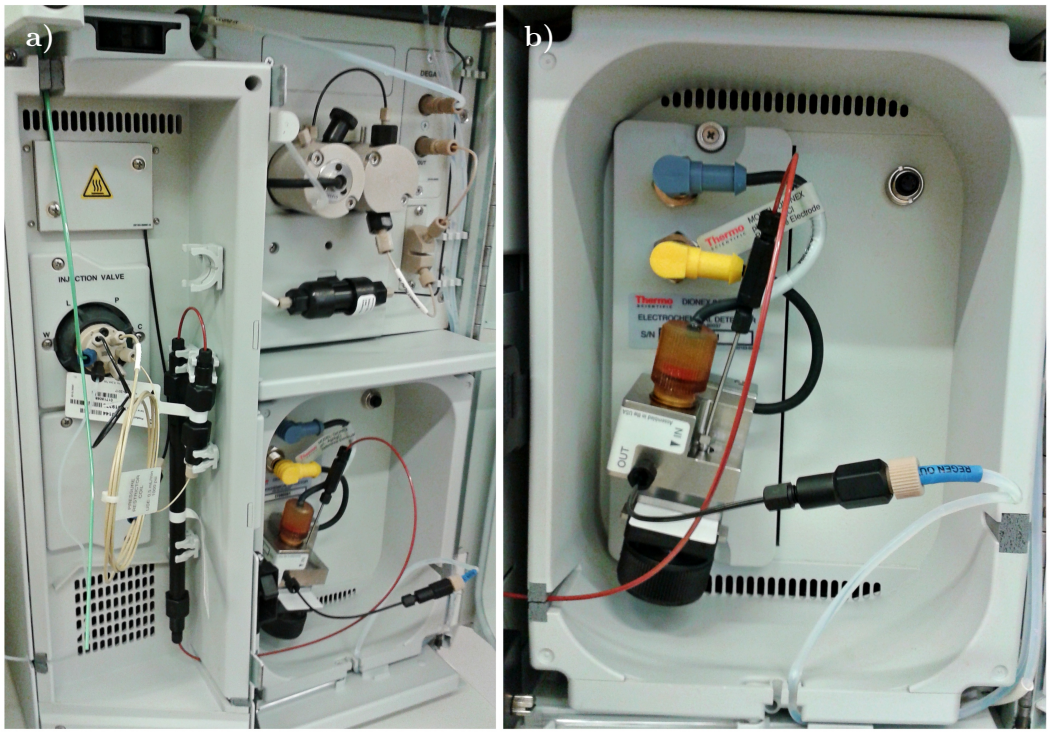

Figure 4.2: a) The Dionex Integrion HPIC system in HPAEC-PAD configuration. b) The correctly plumbed electrochemical detector.

plugging the electrochemical cell into the plug. Close the two cross-headed screws. Remove the torque screw and the dummy electrode from the electrochemical detector. Clean the detector with ultrapure water and put a plastic sealing onto it using the plastic tweezers. Keep in mind that there are different types of seals for the solid gold electrode and the disposable gold electrodes. Put either the solid gold electrode or a disposable electrode onto the detector. Mind directions such that the gold spot of the electrode is placed in the middle of the reaction chamber formed by the sealing. In case of a disposable electrode, put the dummy electrode onto the disposable electrode. Close the detector with the torque screw. Mount the detector to the electrochemical cell. Rinse the Ag/AgCl reference electrode thoroughly with ultrapure water and screw it into the referring place at the electrochemical detector. Tightly seal the KCl container of the reference electrode with parafilm. Connect the capillary leaving the analytical column with the “Eluent In” port of the electrochemical detector. Connect the “Eluent Out” port of the detector with the tube leading to the “Regen In” port of the CR-ATC. In figure 4.2 b) the correctly plumbed electrochemical detector can be seen. Figure 4.2 a) shows the entire HPIC system in HPAEC-PAD configuration. After plugging the black cables with the yellow and the blue connector into the yellow and the blue plug, it can be proceeded with steps 1 to 4 of table 4.1.

To implement the electrochemical detector in the software press `Configure Instrument` in the *Chromeleon Service Manager*. Select `Integrion HPIC System` under `IC` in the directory tree. Make sure that the check boxes `CR-TC` and `Eluent Generator` in the `Electrolytics` tab, as well as the `EDet` check box in the `Detector` tab are ticked. The check boxes `Suppressor` and `CDet` should be unticked. Save the instrument configuration under `File/Save Installation`. Close *Chromeleon Service Manager*, open *Chromeleon 7*, and connect the HPIC device and the autosampler (compare step 6 of table 4.1). Make a consumables inventory as described above.

If a Ag/AgCl reference electrode is used for the first time or if any inconsistency considering the detected pH value turns up, calibrate the reference electrode. To do so, select the `ED` ePanel and follow the instructions under `Calibration`. For the calibration a buffer of pH 7 and one of pH 10 are necessary. During the calibration procedure the reference electrode needs to be unscrewed from the electrochemical cell. This is only possible if the reference electrode's plug is unplugged from the electrochemical cell. For the calibration procedure do not forget to reconnect the reference electrode to the electrochemical cell. If calibration was successful proceed with step 7 of table 4.1.

Prior to removing the electrochemical detector, flush it thoroughly with ultrapure water (for at least 1 h at standard flow rate). Bypass the CarboPac PA20 guard and analytical columns for this step as these columns should not be contacted with ultrapure water only. Switch off the HPIC apparatus. Unplug the connection between the analytical column and the electrochemical detector as well as the connection between the CR-ATC and the detector. Keep in mind that open capillaries and other tubes have to be sealed with dummy plugs. Remove the detector from the electrochemical cell and open the torque screw. Remove the gold electrode and rinse it with ultrapure water before storing it away. Use the plastic tweezers to take of the sealing from the electrochemical detector. Rinse it with ultrapure water and store it away. Put the dummy electrode onto the detector and close it with the torque screw. Unscrew the reference electrode from the detector, clean it with ultrapure water and screw it into the KCl container. Seal the connection between reference electrode and KCl container with parafilm. Seal the electrochemical detector tightly with dummy plugs. Open the two cross-headed screws and unplug the electrochemical cell carefully from its plug.

For the HPAEC-PAD configuration it is necessary to plumb all components between the injection valve and the detector with red PEEK tubing only. All liquid lines should be kept as long as necessary but as short as possible. This is especially important for the tubing between the column and the detector cell. Capillaries of larger diameter than that of red capillaries or longer tubing may decrease peak resolution. Capillaries must not be cut with anything else than the capillary cutter. For the HPAEC-PAD configuration with CarboPac PA20 columns a sample loop with a volume of 10 µL is recommended.

Before installing a new CarboPac PA20 column, scan the background signal. Proceed only if the background signal is below 30 nC. Instructions how to scan

the background signal are given in the column manual. The following installation procedure for the CarboPac PA20 3×30 mm guard column and PA20 3×150 mm analytical column should be followed after any long-term storage (more than one week) or if the column is installed for the first time. Connect only the guard column to the 6-way valve, but not to the electrochemical detector. Flush it for at least 30 min with 100 mmol/L KOH at standard flow rate of 0.5 mL/min. Eluent leaving the guard column is either collected in a beaker glass or a capillary leaving the guard column is directly connected with the "Regen In" port of the CR-ATC. After flushing the guard column is finished, the analytical column can be connected to the guard column. Keep the direction of flow, which is indicated on both columns, in mind. The analytical column is flushed for at least 120 min using the same settings as before. Eluent leaving the analytical column is either collected in a beaker glass or a capillary leaving the guard column is directly connected with the "Regen In" port of the CR-ATC. After flushing is finished the columns have to be equilibrated for 15 min to 25 min using 10 mmol/L KOH. Reconnect the analytical column with the "Eluent In" port of the electrochemical detector and the "Eluent Out" port of the detector with the "Regen In" port of the CR-ATC. Proceed with step 7 of table 4.1. The maximum system pressure with CarboPac PA20 columns is 3500 psi. The typical system pressure however is approximately 2000 psi.

For storing purposes the columns are flushed with 60 mmol/L KOH and tightly capped using black dummy plugs.

Further information on the devices being part of the HPAEC-PAD system, installation and cleaning procedures can be found in their respective manuals. Information and examples concerning separation of various sugars and a comprehensive trouble shooting guide are included in the column manuals [68].

4.3 Checklist for Everyday Operation of HPIC System

The checklist is intended to serve as a quick start guide to start measurements using the Integrion HPIC system. It should help the user to keep the most important steps in mind. However, this checklist does not replace reading the manuals of the components of the HPIC apparatus. Furthermore, this quick start guide represents the consequences drawn from experiences made during the commissioning phase. Therefore, it can slightly deviate from recommendations present in the manuals. In case of uncertainties, follow the instruction given in the official manuals rather than those of this checklist. The checklist can be seen in table 4.1 and is divided into a general section for both HPIC configuration and sections for the two detectors.

Table 4.1: Checklist for starting-up the Integrion HPIC system in HPAEC-sCD or HPAEC-IPAD configuration.

Step	What to do?	Default	Problems, Reasons and Solutions
1	Switch on the PC		IC, HPLC or related instruments are switched on; switch off and restart
2	Log in at PC		
3	Switch on IC and AS-DV Autosampler		
4	Open *Chromeleon Service Manager* and press `Start Instrument Controller`		
5	Start *Chromeleon 7*		
6	Press `Connect` in the `Pump ECD` and `Sampler` ePanels		IC/Sampler not switched on/not yet ready; wait until USB control lights are switched on and retry
7	Refill the eluent bottle with freshly prepared ultrapure water		
8	Open the purge valve and press `Prime` in the `Pump ECD` ePanel		
9	Close the purge valve after purging (is) ended Note: if not stopped manually, purging ends after 300 s		
18	Press `Create` in the *Chromeleon Console* and create an `Instrument Method`, a `Processing Method`, a `Report Template` and a `Sequence` Note: more information concerning these file types and settings can be found in the Chromeleon Quick Start Guide or Chromeleon Help (press `Help` in *Chromeleon Console*)		
19	Press `Monitor Baseline` in the *Chromeleon Console* and wait until the detector signal and the pump pressure are stable		
20	Start a new `Sequence` or resume an existing one to start analysis		
	Suppressed Conductivity Detection		
10	Check which guard and analytical columns are installed e.g.		
	IonPac AS11-HC 2 × 250 mm analytical column	≤ 1800 psi	
	IonPac AG11 HC 2 × 50 mm guard column	≤ 150 psi	
	Typical back-pressure at 30 °C if both columns are connected	≤ 1950 psi	

Step	What to do?	Default	Problems, Reasons and Solutions
11	Set the flow rate to e.g. 0.38 mL/min and switch on the `Pump` in the `Pump ECD` ePanel Note: more information on appropriate flow rates and pressure limits can be found in the column manual [67]	200 psi to 3500 psi	Pressure exceeds limits; loose purge valve/fittings/ferrules, too low/high flow rate, particles trapped in column/capillaries
12	Wait until all tubes (especially CR-ATC) are filled with liquid		Damage of CR-ATC possible
13	Set the concentration to e.g. 10 mmol/L and switch on the `EluentGenerator` in the `Electrolytics` or `Pump ECD` ePanel		EGC 500 KOH cartridge is empty; replace the cartridge
14	Switch on the `CR-ATC` in the `Pump ECD` ePanel		
15	Set the current to e.g. 10 mA and switch on the `Suppressor` in the `Electrolytics` or `Pump ECD` ePanel		
16	Switch on the temperature control `Column TC` in the `Pump ECD` ePanel (column temperature) `Compartment TC` in the `Pump ECD` ePanel (suppressor temp.) `Cell Heater` in the `CDet` ePanel (detector temperature)	 30 °C 20 °C 35 °C	Not controlling the column/detector temperature causes retention time shifts/signal variations, suppressor lifetime is increased at 20 °C
17	Recommendation before starting a measurement: Flush the system with 100 mmol/L KOH for 15 min to remove trace contaminations, equilibrate for 15 min with the KOH concentration present in the beginning of the `Instrument Method` used		
21	Check the background signal Typical background with 1 mmol/L KOH Typical background with 60 mmol/L KOH	 0.5 µS to 1 µS 2.5 µS to 3.5 µS	Contaminated CR-ATC, guard or analytical column, eluent, suppressor or other hardware
	Pulsed Amperometric Detection		
10	Check which guard and analytical columns are installed e.g. CarboPac PA20 3 × 150 mm analytical column CarboPac PA20 3 × 30 mm guard column Typical back-pressure at 30 °C if both columns are connected	 ≈ 2500 psi	
11	Set the flow rate to e.g. 0.5 mL/min and switch on the `Pump` in the `Pump ECD` ePanel Note: more information on appropriate flow rates and pressure limits can be found in the column manual [68]	200 psi to 3500 psi	Pressure exceeds limits; loose purge valve/fittings/ferrules, too low/high flow rate, particles trapped in column/capillaries

Step	What to do?	Default	Problems, Reasons and Solutions
12	Wait until all tubes (especially CR-ATC) are filled with liquid		Damage of CR-ATC possible
13	Set the concentration to e.g. 10 mmol/L and switch on the `EluentGenerator` in the `Electrolytics` or `Pump ECD` ePanel		EGC 500 KOH cartridge is empty; replace the cartridge
14	Switch on the `CR-ATC` in the `Pump ECD` ePanel		
15	Switch on the `ED cell` in the `ED` ePanel		
16	Switch on the temperature control		Uncontrolled column/detector temperature causes retention time shifts/signal variations
	`Column TC` in the `Pump ECD` ePanel (column temperature)	30 °C	
	`Cell TC` in the `Pump ECD` ePanel (detector temp.)	30 °C	
17	Recommendation before starting a measurement: Flush the system with 100 mmol/L KOH for 15 min to remove trace contaminations, equilibrate for 15 min with the KOH concentration present in the beginning of the `Instrument Method` used		
21	Check the background signal		Contaminated column, eluent or other hardware, compromised gold working electrode, wrong settings e.g. wrong waveform selection or reference electrode type
	Typical background with 10 mmol/L KOH at 30 °C	< 30 nC	
22	Always double check if the `Quadruple Waveform` is selected in the `ED` ePanel and in any `Instrument Method` used		Damage of working electrode due to stripping of gold layer; polishing of electrode or replacement

4.4 Trouble History

This section is intended to help users identify troubles that already came up with the present HPIC system and the AS-DV Autosampler. Trouble shooting guides providing a wider variety and greater detail concerning the individual problems and their referring solutions can be found in the column manuals of the IonPac AS11-HC and CarboPac PA20 columns.

Figure 4.3 displays sampling errors for the two different types of vials that can be used with the AS-DV autosampler. Figure 4.3 a) shows a 5 mL vial which was already used for sampling. However, liquid remains around the black cap. In correct operation mode this part of the vial should never be contacted with sample. Figure 4.3 b) shows four 0.5 mL vials. Three of them were sampled correctly as, according to the settings in the `Instrument Method`, the full volume was withdrawn from the vials. In the second vial from the right, there is still some liquid left. This can lead to insufficient rinsing of the sample loop or even lower sample inject volume.

The likeliest cause of such sampling behavior are trapped particles within the sampling line or in the 6-way valve. However, this was ruled out by manually rinsing the sampling line and the inject valve. Furthermore, defects of the sampling head can cause such problems. The reason of the sampling errors which still happen every now and then has not been identified yet. In case of an error the sample was re-injected, if enough sample was present.

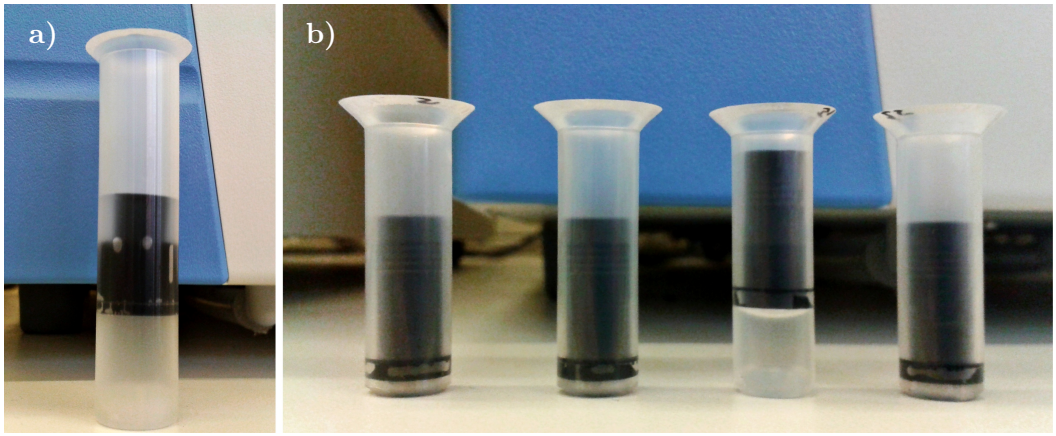

Figure 4.3: Autosampler error for a) a 5 mL vial and b) a 0.5 mL vial (second vial from the right).

Irreversible damage of the CR-ATC was indicated by a crackling noise of the CR-ATC, followed by increased background signal of the conductivity detector. With 1 mmol/L the signal increased from values below 1 µS up to 5 µS. The CR-ATC was replaced and the background was found to be smaller than 1 µS.

Figure 4.4 shows an unidentified signal, recorded during baseline monitoring in the HPAEC-sCD configuration of the HPIC. In this configuration the IonPac AG11-

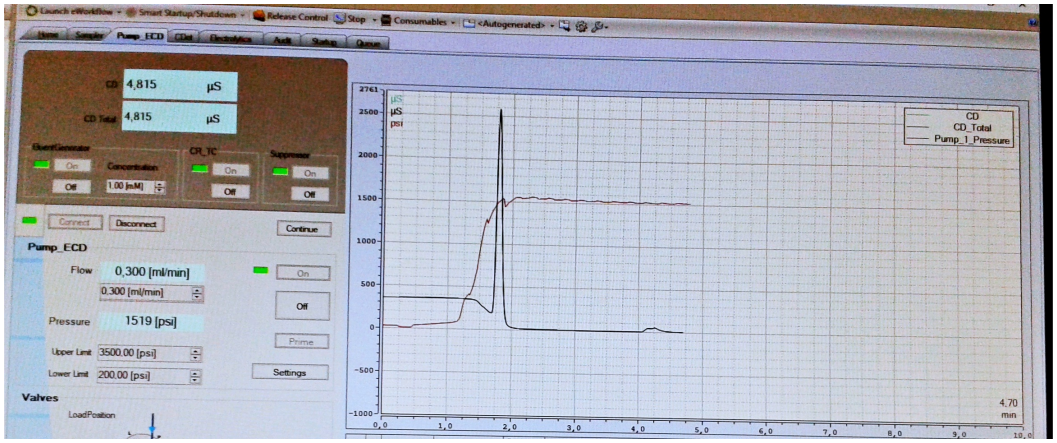

Figure 4.4: Unidentified peak shaped signal, recorded during baseline monitoring.

HC guard and the AS11-HC analytical column were used. This peak results most likely from carbonate contamination that accumulates on the column at low eluent concentrations. Therefore, the system is flushed with 100 mmol/L KOH for approximately 10 min prior to starting a new measurement run. After this cleaning step the column was always equilibrated for 10 min using the setting present in the beginning of the applied `Instrument Method`.

In the HPAEC-IPAD configuration troubles concerning the solid gold electrode turned up. Extremely high background signals in the range of several thousand nC were detected. Under correct operation conditions the background signal should be at least below 50 nC with 10 mmol/L KOH. Opening the detector revealed some kind of fouling of the gold electrode as a black to brownish layer was found on the gold spot. Multiple reasons for this problem are possible, e.g. eluent or system contamination, other waveform selection than the `Quadruple Waveform` and many more. To identify the problem and avoid further damage of the solid gold electrode, disposable electrodes were used from that point on. In figure 4.5 two of the disposable electrodes, which were irreversibly damaged during the problem identification procedure, are shown. In figure 4.5 a) one can see that the gold spot used for sample detection is already partly stripped. Additionally, it is not connected anymore to the larger spot that further transfers the signal to the detection cell. In figure 4.5 b) the small gold spot is already totally stripped. After multiple cleaning procedures and other trouble shooting techniques, a mainboard error and subsequent detector error were identified. After replacing the mainboard, the detector and the fouled solid gold electrode the problem was solved and correct background signals were obtained again.

In figure 4.6 a) a CarboPac PA20 analytical column and one of its frits can be seen. This frit was removed from the column inlet. The position is indicated by the white arrow. It can be seen in the picture that the frit is contaminated with a brownish substance. This contamination may result from eluent or column

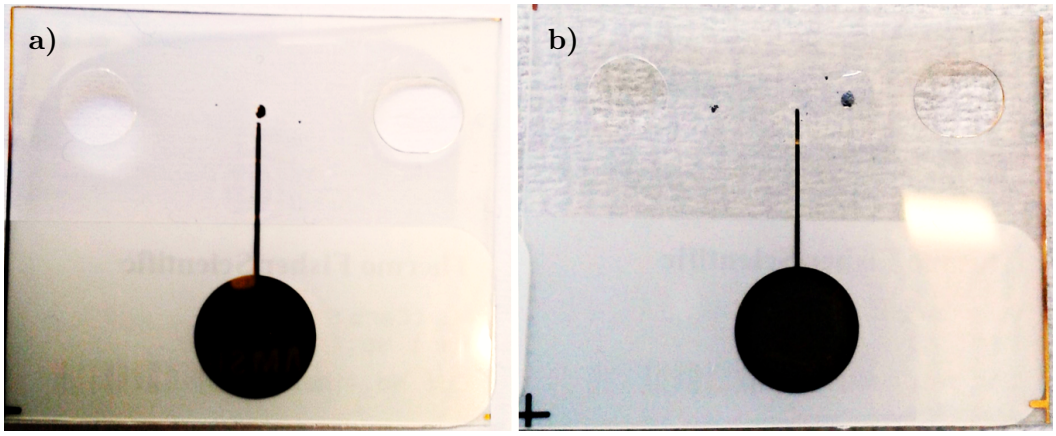

Figure 4.5: a) and b) Examples for irreversibly damaged disposable gold electrodes.

contamination and can lead to high background signals. As the contamination was found on the top of the frit, but not on its underside one can expect that the column material is still clean. However, if the frit of the analytical column is contaminated one can expect that the guard column is already completely contaminated. In the present case, both columns were replaced by new ones. To ease assessing if a frit is considered contaminated, new ones are compared to the dirty one in figure 4.6 b).

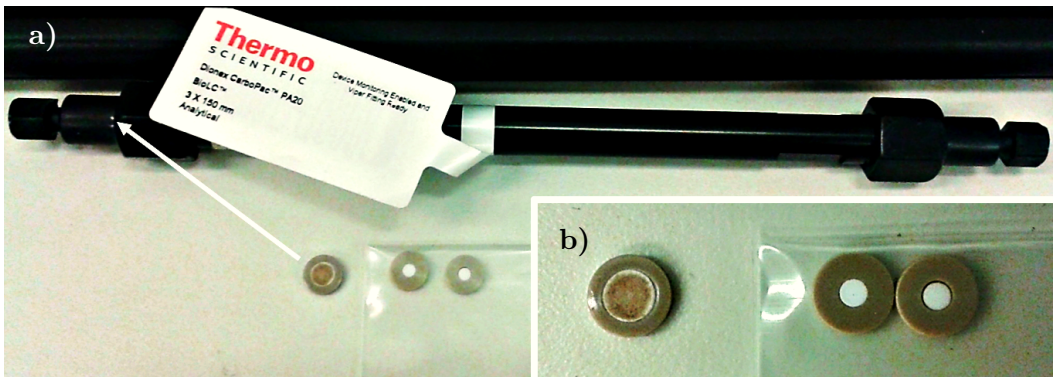

Figure 4.6: a) CarboPac PA20 analytical column with a contaminated frit found at the column inlet. b) Comparison between the contaminated frit and new ones.

5 Results and Discussion

Before electrodialysis experiments could be started an appropriate measurement method for the inorganic and organic acid anions present in black liquor had to be developed. Therefore, this chapter is divided in a part on the measurement method itself and the calibration of the investigated anions and a section on the electrodialysis experiments.

5.1 Simultaneous Analysis of Inorganic and Organic Anions

In figure 5.1 the chromatogram of the 5 mg/L mix standard is depicted. Additionally, the profiles of the KOH gradient, used as eluent, as well as the profile of the suppressor current can be seen. The suppressor current is adjusted according to the concentration gradient. However, the suppressor needs more time to react and current adjustments are performed such that this fact is taken into account.

The chromatogram shows that anions carrying one negative charge are eluted earlier than anions carrying two or more charges.

Comparing the monovalent organic anions lactate, acetate, glycolate and formate, it is a bit more difficult to find an explanation for their elution behavior. However, the concept of charge density of the ions can be applied here. Acetate is larger than formate. Therefore the charge density of formate is higher and acetate elutes earlier than formate. The same principle applies for lactate and glycolate. Lactate is larger than glycolate and therefore lactate elutes first. Glycolate and acetate could not be separated from each other. This might be because of their similar size and charge density.

The elution order of oxalate and succinate can also be explained by the size and subsequently the charge density of the two ions. Oxalate is smaller and has a higher charge density. Therefore it elutes later than succinate. According to literature the retention time for dicarboxylic acids increases if their pK_avalues decrease. This applies for oxalic and succinic acid too. The pK_avalues for oxalic acid are 1.27 and 4.29; the corresponding values for succinic acid are 4.21 and 5.64 [22].

The inorganic anions chloride, carbonate, sulfate and phosphate follow the principle of charges. Monovalent anions elute earlier than di- and trivalent anions. However, the overall order of organic and inorganic anions depends also on multiple system factors, e.g. the column material and the profile of the concentration gradient. Therefore, straightforward prediction of the elution order is not always possible. For the identification of each anion single standards were used and the retention times of the referring anion were assigned to a peak in the mix standard.

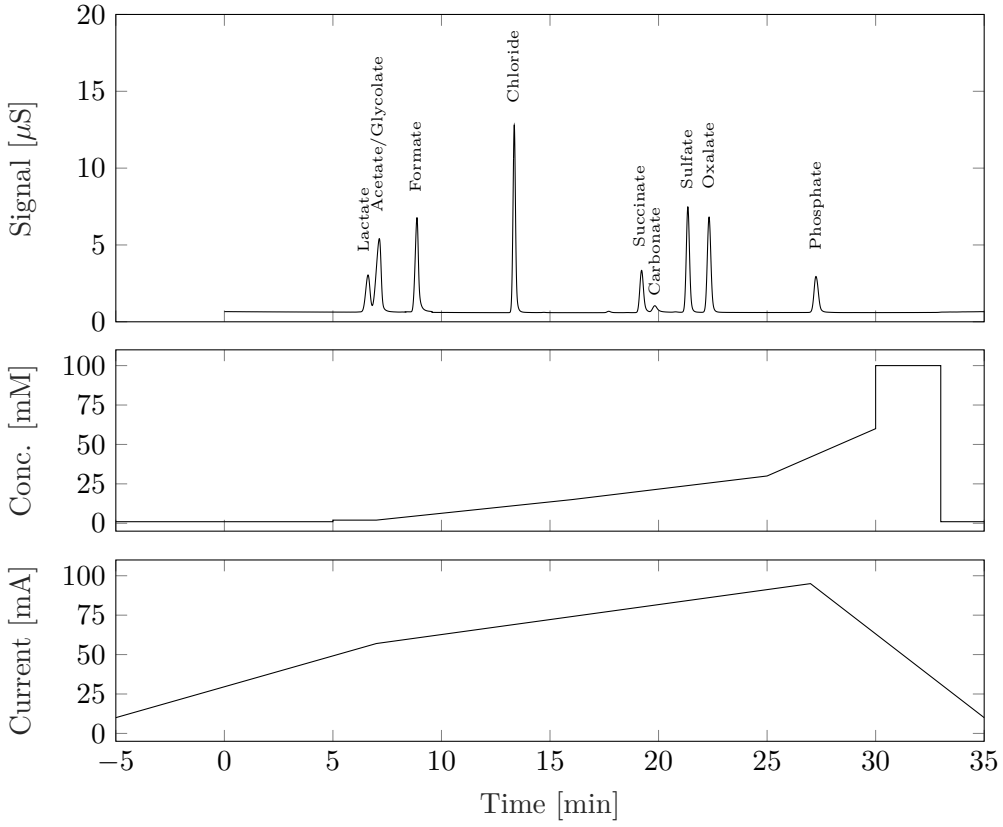

Figure 5.1: Instrument method and resulting chromatogram for the simultaneous analysis of various inorganic anions and organic acid anions using HPAEC-sCD.

5.1.1 Calibration

External standard calibration was performed for lactate, acetate, glycolate, formate, chloride, succinate, carbonate, sulfate and phosphate. Between five and eight standard solutions of different concentrations were analyzed to determine the calibration function of each anion. All measurements were performed in duplicates. In table 5.1 the results of the compound-specific calibration functions are shown. All of them are of type linear equation with offset. Quantification was done using the peak area.

Lactate and the coeluting compounds acetate and glycolate could only be calibrated in the range between 1 and 15 mg/L. Above this concentration range separation of the two peaks was impossible. Within this range the coefficient of determination R^2 indicates good linearity for lactate and the sum of acetate and glycolate.

Formate gives a sharp peak and its retention time is sufficiently long to not interfere with acetate/glycolate. Therefore, it was possible to calibrate it over the full concentration range of 1 mg/L to 50 mg/L. Linearity is good and the relative

Table 5.1: Data of the compound-specific calibration functions. Ac/Glyc stands for acetate/glycolate. All functions are of type linear equation with offset. RSD is the relative standard deviation and R^2 is the coefficient of determination.

Substance	Time [min]	Conc. Range [mg/L]	[mg/L]	RSD [%]	R^2	d [µS min]	k [µS min L/mg]
Lactate	6.467	1	15	1.92	0.999	0.0269	0.1085
Ac/Glyc	7.011	1	15	3.58	0.997	0.1601	0.2232
Formate	8.900	1	50	3.72	0.999	0.2491	0.196
Chloride	13.443	1	50	2.31	0.999	−0.0146	0.3444
Succinate	19.323	1	50	7.31	0.994	0.2327	0.0696
Carbonate	19.934	1	50	24.49	0.645	0.137	0.0039
Sulfate	21.443	1	50	2.12	0.999	−0.0149	0.2504
Oxalate	22.330	1	50	5.10	0.997	0.3148	0.1917
Phosphate	27.273	1	50	2.34	0.999	−0.0076	0.1148

standard deviation RSD is considered to be low with a value of 3.72 %.

The same is true for chloride, succinate, sulfate, oxalate and phosphate. Carbonate, however, does not show conformance with a linear calibration function. Additionally, the relative standard deviation is far too high to be able to reliably quantify carbonate within an unknown sample. There are basically two explanations for this behavior. On the one hand carbon dioxide present in the air can dissolve in ultrapure water and contaminate the eluent and the samples, as the vial cap is not completely closed. In [22] it is discussed that inorganic contaminants present in the eluent are retained at the stationary phase, if gradient concentration is low. When the concentration is raised the contamination is washed off. However, it can interfere with compounds of interest or increase the detected amount of a species. On the other hand, carbonate is not fully protonated in the suppressor but is partly present as HCO_3^- and H_2CO_3. Therefore, detection of carbonate is extremely difficult. In all further measurements carbonate is only analyzed qualitatively but not quantitatively.

5.1.2 OnGuard II Ag Cartridge Recovery Experiment

OnGuard II Ag cartridges were used to remove high amounts of chloride from the samples. To evaluate if and to which extent the other calibrated anions are lost by this sample preparation procedure, a recovery experiment was performed. Standards of different concentrations were measured with and without treatment by an OnGuard II Ag cartridge. The results of this experiment are shown in table 5.2. All standards, treated and untreated ones, were measured in duplicates. The recovery rate is calculated using the two arithmetic mean values.

Lactate and acetate/glycolate were calibrated from 1 mg/L to 15 mg/L. Therefore, only three different standards were evaluated for the recovery rates of these

Table 5.2: Recovery rates of inorganic and organic anions after treatment with an OnGuard II Ag cartridge at a flow rate of 2 mL/min; n.d. means not detectable.

Conc. [mg/L]	Lac [%]	Ac/Glyc [%]	For [%]	Cl^- [%]	Succ [%]	SO_4^{2-} [%]	Ox [%]	PO_4^{3-} [%]
1	100.16	103.84	136.54	n.d.	n.d.	96.52	n.d.	100.65
5	100.33	100.00	91.86	0.96	103.36	101.40	101.38	100.59
10	100.44	100.34	99.55	n.d.	101.06	100.67	100.51	99.78
50	-	-	100.11	0.06	102.48	101.82	100.36	101.75

anions. However, in the range from 1 mg/L to 10 mg/L neither lactate nor acetate/glycolate was lost by the sample preparation procedure. Deviations of 5 % in both directions are most likely a result of pipetting errors.

Formate concentrations were found to vary strongly from the values expected for the first two samples, containing 1 mg/L and 5 mg/L. The other two samples deviated only slightly from 100 % recovery. Therefore the formate concentration determined from an unknown sample treated with an OnGuard II Ag cartridge should be larger than 10 mg/L.

Chloride was efficiently removed by the OnGuard II Ag cartridge. It was either not possible to detect this anion in the sample, or the detected amount was smaller than 1 % of the amount present in the untreated sample.

Sulfate and phosphate concentrations were also not significantly affected by the sample pretreatment procedure. The recovery rates of both anions ranged from 96.52 % to 100.81 %.

Similar behavior was observed for succinate and oxalate. However, both ions could not be detected in the 1 mg/L samples. Therefore, unknown samples treated with OnGuard II Ag cartridges need to contain more than 5 mg/L succinate and oxalate, for evaluation.

5.2 Electrodialysis

Feasibility of the electrodialytic recovery of organic acids from black liquor was first investigated using a black liquor model solution. After successfully conducting two experiments using this solution, another two experiments using diluted black liquor were carried out. All four experiments were performed at constant voltage of 10 V. The produced current is recorded and the experiment is evaluated with regard to the electric power of the apparatus. Figure 5.2 shows the behavior of the electric power during each of the four experiments.

Power increased until a plateau was reached in both experiments conducted with black liquor model solution. The appearance of these two curves is similar. However, the starting and end values deviate from each other. The power, and therefore the transported current, is higher throughout the first experiment. Additionally,

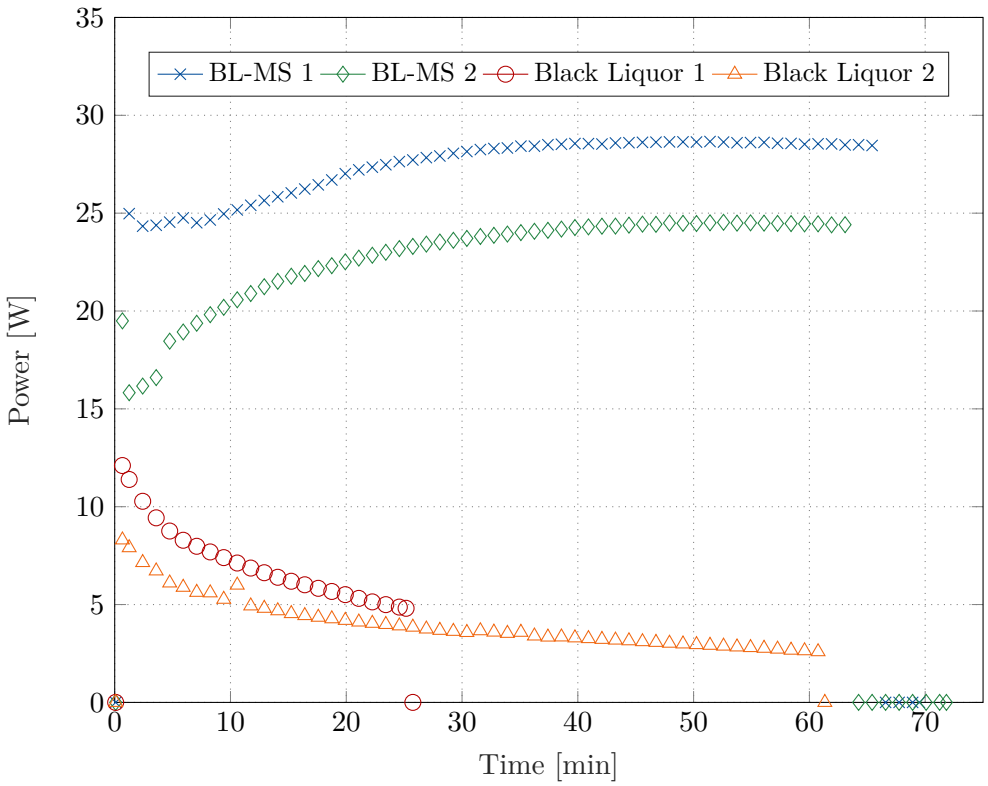

Figure 5.2: Electric power during the electrodialysis experiments at constant voltage of 10 V with black liquor model solution (BL-MS) and diluted black liquor.

the difference between the starting and end value is smaller in the first experiment than in the second experiment.

As the voltage is kept constant throughout the experiments, the only variable that affects the electric power is electric current. Power is directly proportional to current. Current itself, is inversely proportional to resistance. The electric current increases throughout both experiments with black liquor model solution. Conversely, this means that the electrolyte's resistance decreases. The resistance of an electrolyte decreases with rising temperature, because of the higher mobility of ions. On the other hand, the resistance of an electrolyte increases if ions get depleted. During both experiments the temperature of all liquid streams is observed to increase. The rising power is most likely a consequence of this rise in temperature. Additionally, the plateaus indicate that at the end of the experiments, the electrolyte still contains enough ions to keep the power of the electrodialysis apparatus constant. The difference between the first and the second experiment with black liquor model solution may be explained by deviating ion concentrations in the beginning of the experiment.

Diluted black liquor showed completely different power profiles than observed

for the experiments on black liquor model solution. Power, and therefore electric current, decreased during both experiments. This indicates an increase in the electrolyte's resistance. Increasing resistance can be explained by ion depletion from the diluted black liquor stream. Temperature of all liquid streams increased during both experiments. However, the increase in temperature seemed to be too low to counteract the effect of ion depletion. Additionally, lignin present in black liquor might adsorb on the ion-exchange membranes and hinder ion transportation. This layer would also result in higher resistance and lower current.

Further measurements were conducted to assess the progress of the electrodialytic recovery of organic acids from the model solution and diluted black liquor.

5.2.1 Electrodialytic Treatment of Black Liquor Model Solution

Figure 5.3 shows the course of the pH values of samples withdrawn from the acid, base and salt compartments of the electrodialysis. All samples were measured at 25 °C to avoid influence of the temperature rise observed during the experiment.

It can be seen that the pH of the base compartment rises following a similar course in both experiments. During the first experiment the pH value of the base compartment rose by 1.1 pH units and during the second experiment an increase of 0.9 pH units was measured. In the acid compartment a drop in pH of 0.8 pH units could be observed between the first and the last sample of the first experiment. During the second experiment the pH value of the acid compartment dropped by 0.3 pH units. This indicates that more acid molecules were accumulated during the first experiment. However, in the first experiment too many NaOH pellets were added to the feed solution. Therefore, some concentrated HCl was used to adjust the pH from 14 to 13. Chloride present as NaCl in the salt compartment is efficiently transported through the electrodialysis membranes. Moreover, it forms the strong acid HCl in the acid compartment. The presence of comparatively large quantities of HCl in the acid compartment explains the deviation between the first and the second experiment. In the second experiment no HCl had to be added to the feed.

The pH value of the feed solution behaves similar in both experiments. The total decrease measured between the first and the last feed sample was 0.2 pH units for the first experiment and 0.3 pH units for the second one. The deviation between the initial values results from the different amount of NaOH pellets added to the feed.

Additionally, the accuracy of the pH electrode has to be questioned. Before starting both experiments the acid and the base compartment were filled with 10 mmol/L of HCl and NaOH respectively. The theoretical pH values of these two solutions are 2 and 12. Even though the electrode was freshly calibrated before each measurement series, pH values differed by approximately 0.5 pH units from the theoretical values. Deviations from pH 13 in the feed before the experiment was started might result from inaccuracies of the pH electrode or the pH indicator paper. Another possible explanation is that the solutions filled into the compartments are

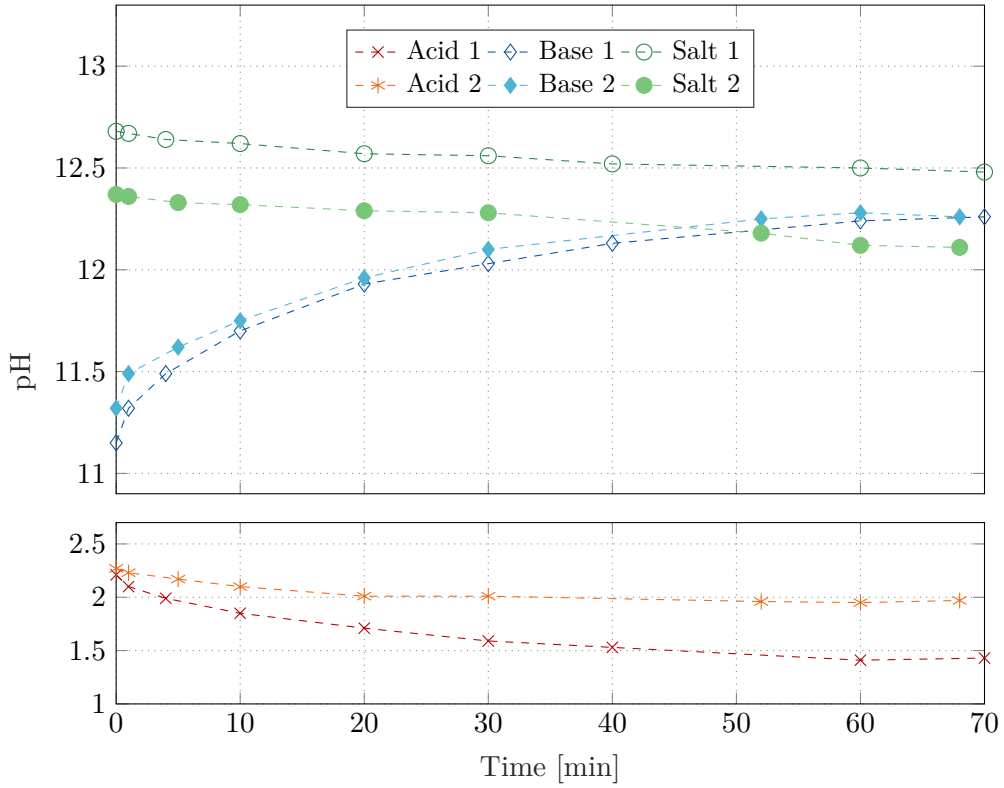

Figure 5.3: pH values of samples withdrawn from the acid, base and salt compartment during the two electrodialysis experiments with black liquor model solution. Measurements were performed when samples showed a temperature of 25 °C.

diluted by deionized water or storage solution trapped inside the tubes or pumps of the electrodialysis apparatus.

The conductivity measurement performed as a consequence of this observation should elucidate the problem. The results, which could only be recorded for the second experiment, are shown in figure 5.4.

The conductivity of the base compartment could be compared to values measured with different dilutions of NaOH. At 25 °C the conductivity of 10 mmol/L, 50 mmol/L, 100 mmol/L and 500 mmol/L sodium hydroxide solutions is 2.79 mS/cm, 13.5 mS/cm, 26.5 mS/cm and 114.8 mS/cm. Assuming a linear correlation, the measured conductivity value at time 0 of 2.45 mS/cm refers to a NaOH concentration of around 9 mmol/L. The pH value of the same sample however was only 11.32 , which refers to a concentration of approximately 2 mmol/L NaOH. The pH of the base after finishing the experiment was 12.26 referring to a concentration of 18 mmol/L NaOH. The conductivity of the same sample was 28.8 mS/cm. This indicates a NaOH concentration of 125 mmol/L. The conductivity and the pH electrode cannot be compared as their results differ strongly.

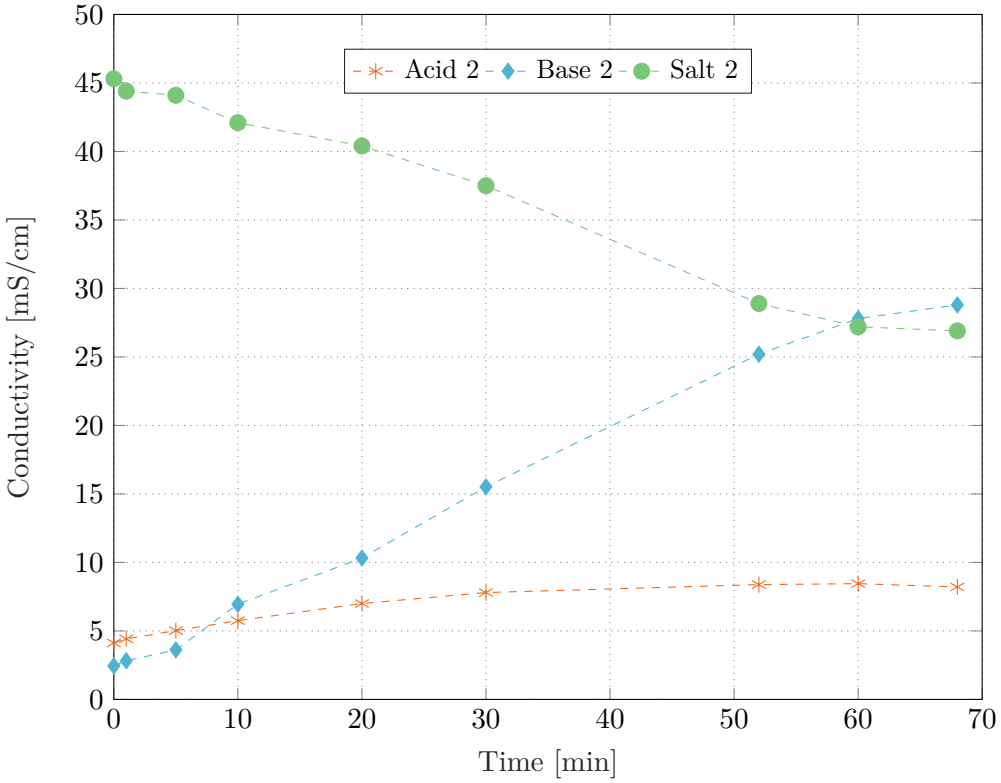

Figure 5.4: Conductivity of samples withdrawn from the acid, base and salt compartment during the second electrodialysis experiment with black liquor model solution. Measurements were performed when samples showed a temperature of 25 °C.

For the acid and salt compartment it is not possible to correlate the conductivity with a concentration as multiple ions are present. However, these curves show the expected profile (compare figure 5.4). The conductivity in the salt compartment decreases due to ion depletion. At the same time, the conductivity of the acid compartment increases because of the enrichment of ions. Higher conductivity as a result of increasing concentration is also observed for the base compartment.

To qualitatively and quantitatively determine which organic and inorganic anions are transported into the acid compartment, ion chromatographic analysis was performed. Salt and base compartment were cross-checked and mass balances were calculated for each time step. In the base compartments anions other than carbonate could not be detected. The results of the ion chromatography measurements are displayed in figure 5.5 and figure 5.6. The results of the mass balances for the detected anions can be seen in table 5.3.

In the acid compartment of both experiments on black liquor model solution lactic acid, formic acid and acetic acid are accumulated to unequal extents. Increases

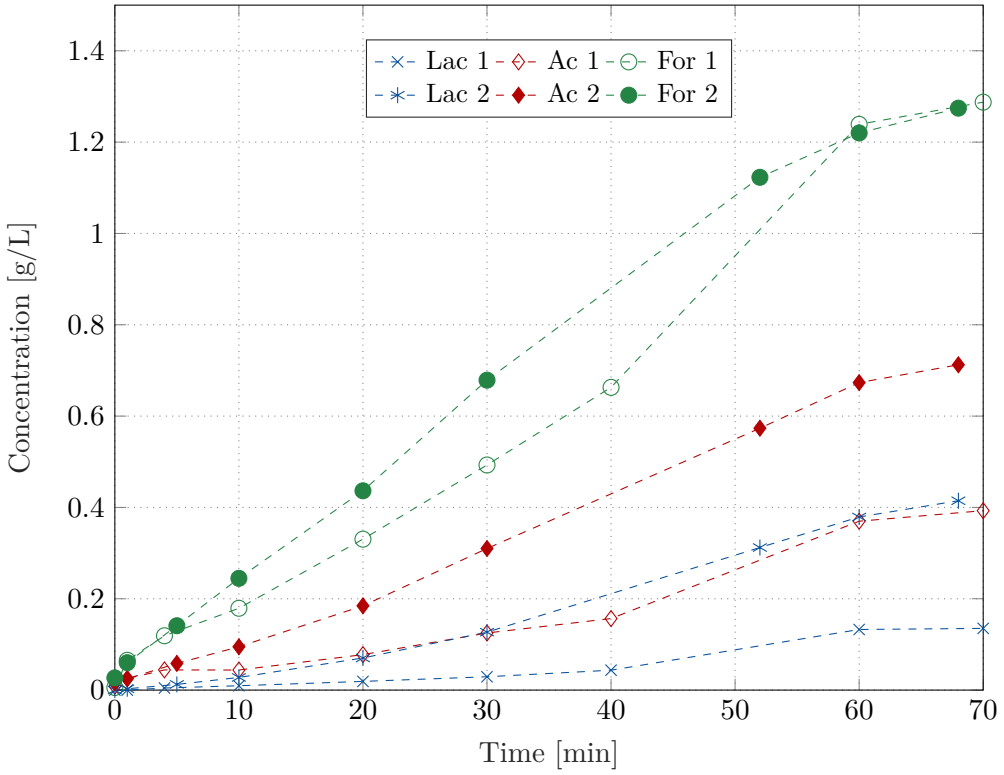

Figure 5.5: Concentration of short organic acid anions in samples withdrawn from the acid compartment during the two electrodialysis experiments with black liquor model solution.

of 1.28 g/L and 1.25 g/L of formic acid were detected during the first and the second experiment. 0.39 g/L and 0.70 g/L of acetic acid were measured in the respective cases. At the end of the experiments, with around 0.14 g/L and 0.42 g/L the lowest amounts were found for lactic acid. Interestingly, in the first experiment less lactic and acetic acid was transported compared to the second experiment. Formic acid concentrations lagged behind in the beginning, but the last two samples showed approximately the same concentration as the last two samples of the second experiment. As the pH drop was 0.5 pH units larger in the first experiment it is assumed that the transport of chloride is preferred over the transport of the organic anions like acetate or lactate. Formate, which is the smallest of the present organic anions, was not affected.

As the acid samples have to be treated with the OnGuard Ag II cartridge, quantification of chloride in the acid compartment was not possible. However, in the salt compartment chloride depletion could be observed during the first experiment (compare figure 5.6). Anions other than lactate, acetate and formate could not be detected in the acid compartment of both experiments.

In figure 5.6 the anion concentrations detected in the salt compartment during

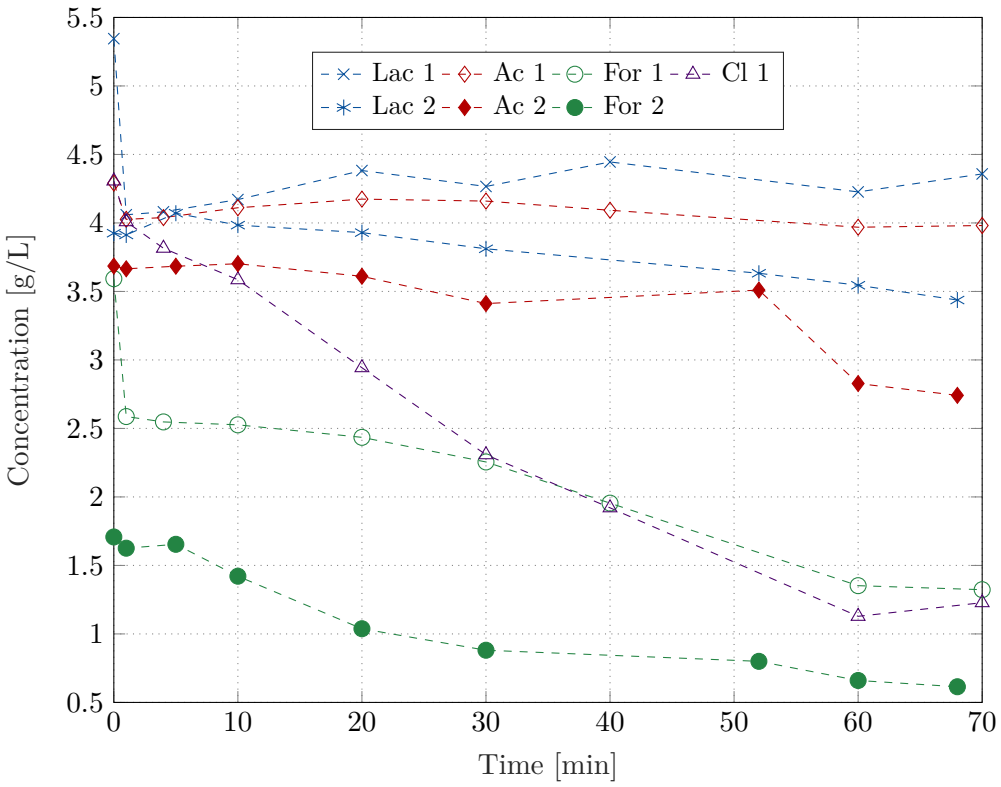

Figure 5.6: Concentration of short organic acid anions and chloride in samples withdrawn from the feed compartment during the two electrodialysis experiments with black liquor model solution.

electrodialytic treatment of black liquor model solution are displayed. The concentrations of lactate, acetate, formate and chloride present in the feed of the first experiment before switching on the current were 5.35 g/L, 4.29 g/L, 2.27 g/L and 4.31 g/L respectively. In the second experiment 3.93 g/L, 3.69 g/L and 1.71 g/L were measured for lactate, acetate and formate. Chloride was not detected. No explanation for this deviation could be found.

During the first experiment lactate depletion of 0.99 g/L was determined. The acetate, formate and chloride concentrations dropped by 0.31 g/L, 2.27 g/L and 3.08 g/L between the first and the last feed sample. In the second experiment the concentrations of lactate, acetate and formate decrease by 0.49 g/L, 0.95 g/L and 1.1 g/L respectively. As no chloride was present in the salt compartment only organic anions could be transported during the second experiment. The smaller pH drop in the acid compartment during this experiment can be explained with the fact that only weak organic acids were present in the solution.

In the first experiment lactate and formate showed the largest concentration drop between the start of the experiment and 1 min afterwards. As this initial decrease

Table 5.3: Results of the mass balance of short organic acid anions during the two electrodialysis experiments with black liquor model solution. The initially measured concentration was taken as 100 %.

Black Liquor Model Solution 1				Black Liquor Model Solution 2			
Time [min]	Lactate [%]	Acetate [%]	Formate [%]	Time [min]	Lactate [%]	Acetate [%]	Formate [%]
0	0	0	0	0	0	0	0
1	−24.05	−5.78	−22.05	1	−0.27	−0.33	−2.81
4	−23.56	−5.04	−21.71	5	4.07	1.08	3.49
10	−21.79	−3.37	−20.81	10	2.18	2.56	−3.94
20	−17.65	−1.13	−19.41	20	1.87	2.50	−15.00
30	−19.64	−0.36	−19.81	30	0.31	0.63	−10.08
40	−16.02	−1.18	−22.85	52	0.51	11.04	10.86
60	−18.45	0.90	−23.47	60	0.00	−4.42	8.40
70	−15.95	1.72	−23.02	68	−1.83	−5.28	8.89

was not observed during the second experiment, it is assumed that an equilibration effect of the brand-new ion-exchange membranes takes place. Leakage between the salt compartment and another compartment is unlikely as this would lead to a constant concentration decrease over the full experimental time.

The mass balances established took the concentrations of those anions into account which could be determined in all compartments. This means that chloride could not be balanced as this ion was removed during sample pretreatment using the OnGuard II Ag cartridges. For the experiments performed on black liquor model solution lactate, acetate and formate concentrations were determined in the acid, base and salt compartment. In the base compartment, none of the three acid anions was found. The sum of the concentrations detected in the acid and salt compartment before the experiment was started was assumed to be 100 %. Any deviation from this value is considered to be the result of a loss or experimental error.

Lactate and formate show higher losses than acetate in the first experiment. Approximately 20 % to 25 % of lactate and formate cannot be detected compared to the initially present amount. Additionally, the loss between the start of the experiment and 1 min afterwards is tremendously high. As this behavior cannot be reproduced during the second experiment, this may indicate a membrane equilibration effect. However, the fact that acetate does not seem to be prone to this effect contradicts this idea.

During the second experiment mass balances show errors between 0.31 % and 15 %. The present deviations can have multiple reasons. Pipetting errors and generally small losses during sample preparation for ion chromatography analysis may contribute. Another possible reason is a small volume change in the compartments.

Even though, this was not noticeable by eye, ions transport their hydration shell from one to the other compartment. This changes the volumetric concentration depending on the extent of volume change. In future experiments the volume of the single compartments present at the end of the experiment should be determined and mass balances should be adjusted for volume changes.

5.2.2 Electrodialytic Treatment of Diluted Black Liquor

The experiments on black liquor model solution showed the general feasibility of organic acid accumulation in the acid compartment. Simultaneously sodium hydroxide was concentrated in the base compartment. Therefore, the electrodialytic recovery of organic acids and cooking chemicals was further investigated with diluted black liquor. Dilution with deionized water was necessary as the total dry substance content of the black liquor was 41.6 %. To protect the ion-exchange membranes from damages a total dry substance content of 5 % was chosen. Two experiments were performed and both of them were evaluated with respect to pH and conductivity, accumulation and depletion of anions in the acid compartment and the salt compartment, as well as a mass balance.

In figure 5.7 the pH values determined from samples withdrawn from the acid, base and salt compartment are shown. All samples were measured at 25 °C to avoid influence by the temperature rise observed during the experiment.

The first experiment had to be terminated after 25 min as dangerously high amounts of H_2S were measured. In contrast to the experiments performed with black liquor model solution, diluted Kraft black liquor contains the cooking chemicals NaOH and Na_2S. Together with the other anions, negatively charged sulfide is transported across the anion-exchange membranes and enters the acid compartment where it forms toxic H_2S at pH values below 7.

During the second experiment small volumes of concentrated NaOH were added to the base compartment to keep the H_2S level under control. Additionally, the base compartment was filled with 10 mmol/L NaOH to avoid H_2S emerging immediately from the acid compartment. This is the reason why the initial pH value of the solution withdrawn from the acid compartment is between 11 and 11.5 for both experiments. After 10 min and 43 min NaOH was added, leading to a pH increase. Decreasing pH values between these points result from the accumulating acids.

The pH of the base compartment rises from 2 to 11.2 in the first experiment. The low pH in the beginning is caused by the fact that 10 mmol/L HCl were added instead of 10 mmol/L NaOH. The rise in pH results from the accumulation of NaOH in the course of the experiment. In the beginning of the second experiment the base compartment was filled with 10 mmol/L NaOH. Therefore the initial pH value was 11.5. Small deviations from expected pH values either result from electrode inaccuracy or dilution by dead volume trapped inside the pumps or membranes. In the course of the experiment the pH increased from 11.5 to 12 due to the accumulation of NaOH.

The pH of samples withdrawn from the salt compartment neither changed in the

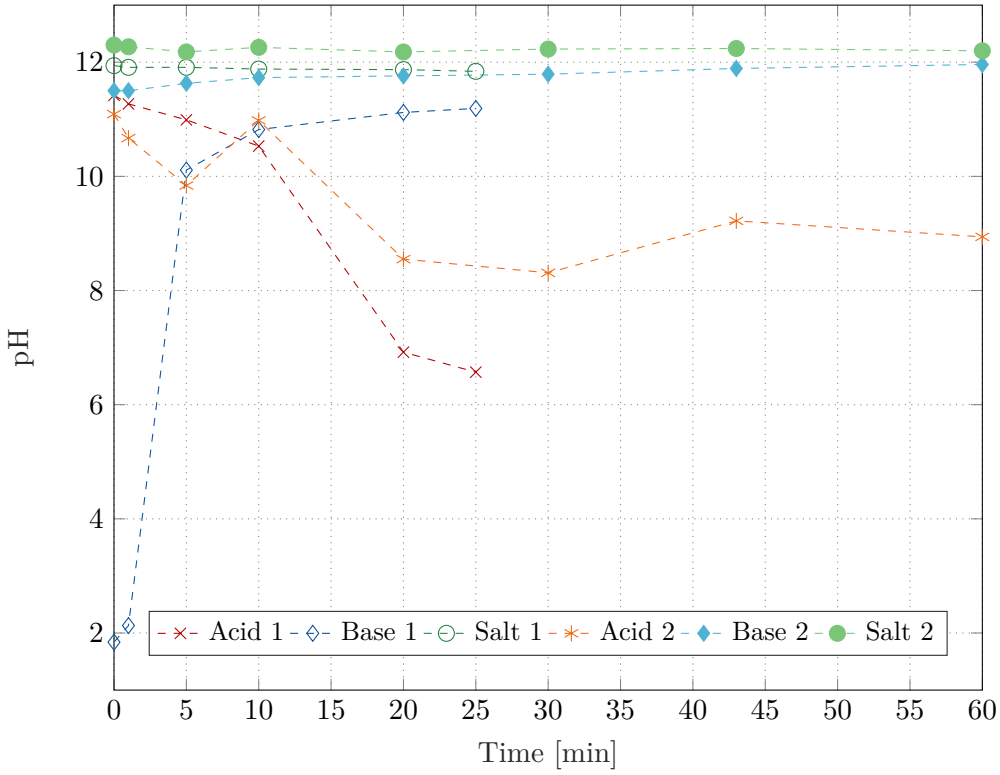

Figure 5.7: pH values of samples withdrawn from the acid, base and salt compartment during the two electrodialysis experiments with diluted black liquor. Measurements were performed when samples showed a temperature of 25 °C.

first nor in the second experiment. This is most likely due to the buffering effects of lignin present in black liquor.

In figure 5.8 the conductivity values over time for each compartment are shown. All samples were measured at 25 °C to avoid temperature influence. The salt compartment containing diluted black liquor shows values fluctuating around 30 mS/cm for the first experiment. The reduction of ions over the course of the experiment seems to be small enough to not affect the overall conductivity of the solution. In the second experiment the conductivity slightly decreases from 31.3 mS/cm to 28.4 mS/cm. However, if this is a conductivity change or a measurement inaccuracy cannot be determined.

The conductivity in the base compartment drops from 3.64 mS/cm to 2.34 mS/cm in initial phase of the experiment (from 0 min to 5 min). This might be due to the fact that the present HCl and NaOH form water and NaCl which is less conductive than free H_3O^+ or OH^- ions. Later in the experiment NaOH accumulates in the base compartment, which can also be seen in the pH change from an acidic to an alkaline pH (compare figure 5.7). Therefore, free OH^- ions are predominantly present and raise the conductivity of the solution from 2.34 mS/cm to 3.77 mS/cm. In the second

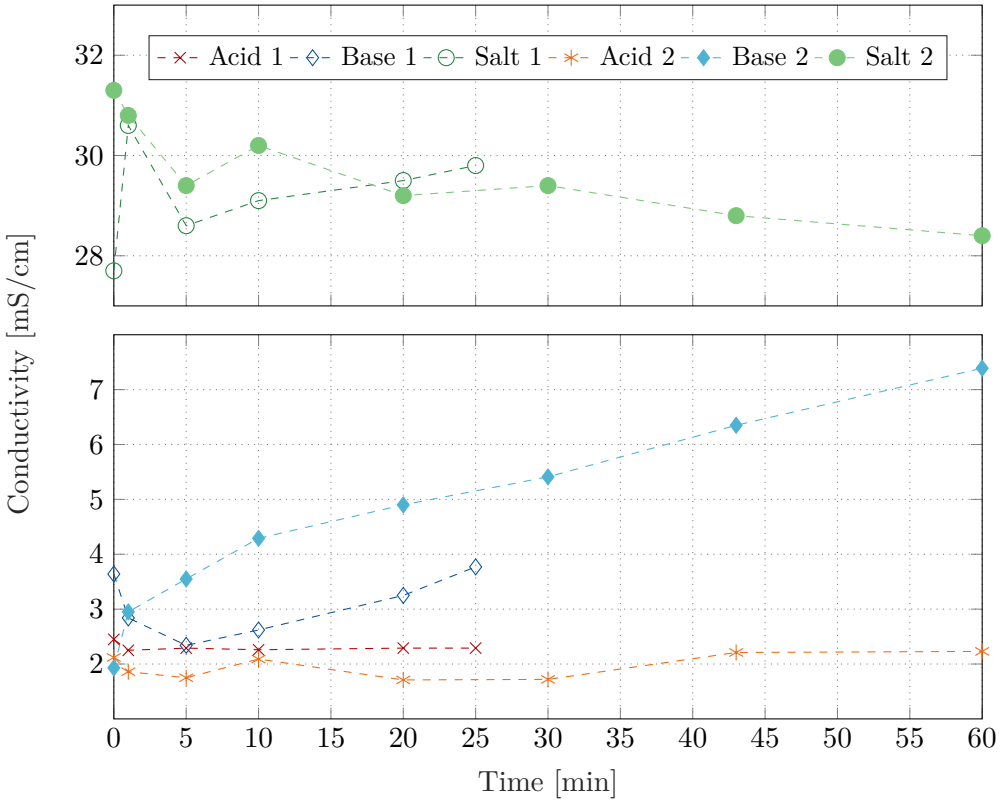

Figure 5.8: Conductivity of samples withdrawn from the acid, base and salt compartment during the two electrodialysis experiments with diluted black liquor. Measurements were performed when samples showed a temperature of 25 °C.

experiment NaOH was solely present in the beginning of the base compartment. The conductivity of approximately 2 mS/cm indicates a concentration of a little bit less than 10 mmol/L. As the molar conductivity of OH^- ions is smaller than that of H_3O^+ ions, it can be explained why the initial conductivity value of the base differed between the first and the second experiment.

The acid compartment contains 10 mmol/L NaOH in the beginning of both experiments. This fits to the measured conductivity values of 2.45 mS/cm and 2.12 mS/cm. As the transport of anions and H_3O^+ into the acid compartment mainly leads to the formation of salt and water almost no change in conductivity can be observed for both experiments.

To be able to comment on the extent of anion transport across electrodialysis membranes, ion chromatography measurements were performed. The results for samples withdrawn from the acid compartment are displayed in figure 5.9. Results for the salt compartment can be seen in figure 5.10.

Lactate, acetate or glycolate, formate and chloride could be identified in the acid compartment during the first experiment with diluted black liquor. Acetate

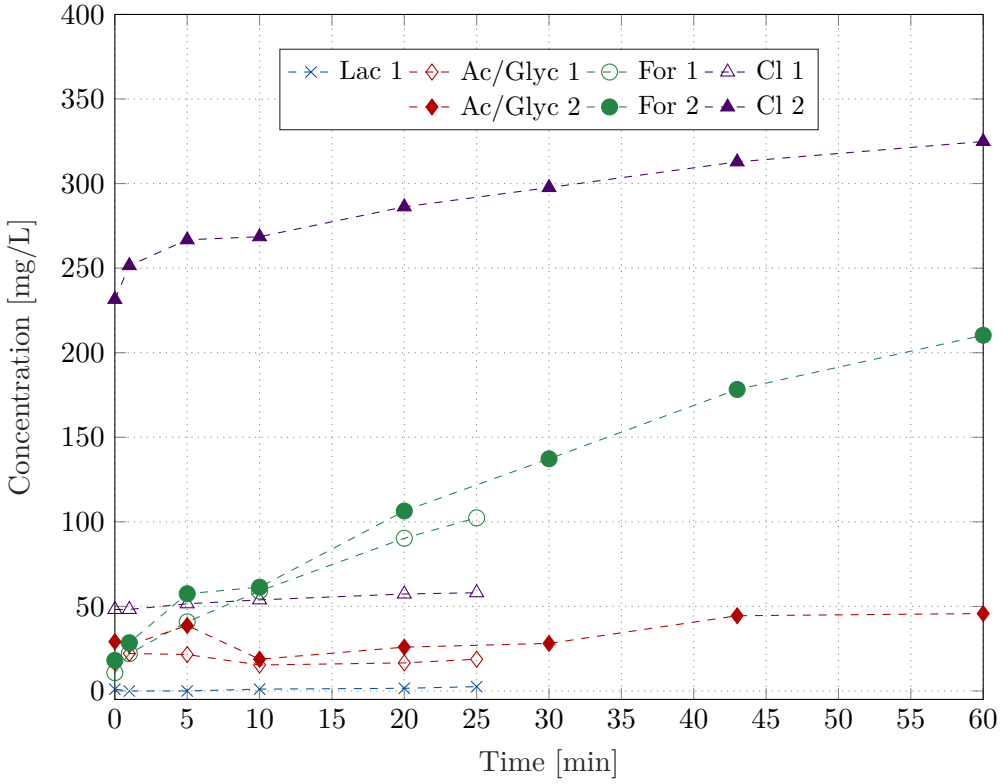

Figure 5.9: Concentration of short organic acid anions and chloride in samples withdrawn from the acid compartment during the two electrodialysis experiments with diluted black liquor.

or glycolate, formate and chloride were also detected in the second experiment. Lactate, however, could not be found. Anions other than the ones displayed could not be detected in the acid compartment for any of the two experiments.

The accumulation rates of formate and the sum of acetate and glycolate were similar in the two experiments. Formate showed the highest accumulation rates of of all anions with 3.66 mg/(L min) in the first experiment and 3.20 mg/(L min) in the second experiment. This indicates that smaller anions were preferably transported. Compared to formate, the lactate transportation rate was low, as the initially present concentration of 1 mg/L raised to 2.55 mg/L within 25 min. This means that 1.55 mg/L lactate moved from the feed to the acid compartment, which refers to a transportation rate of 0.06 mg/(L min). The remaining lactate is most likely some impurity from previous experiments. None zero starting values for the other anions are also considered to result from carry-over.

For chloride the transportation rate deviated strongly between the two experiments. In the first experiment 0.4 mg/(L min) of chloride moved from the salt compartment to the acid compartment. During the second experiment, however,

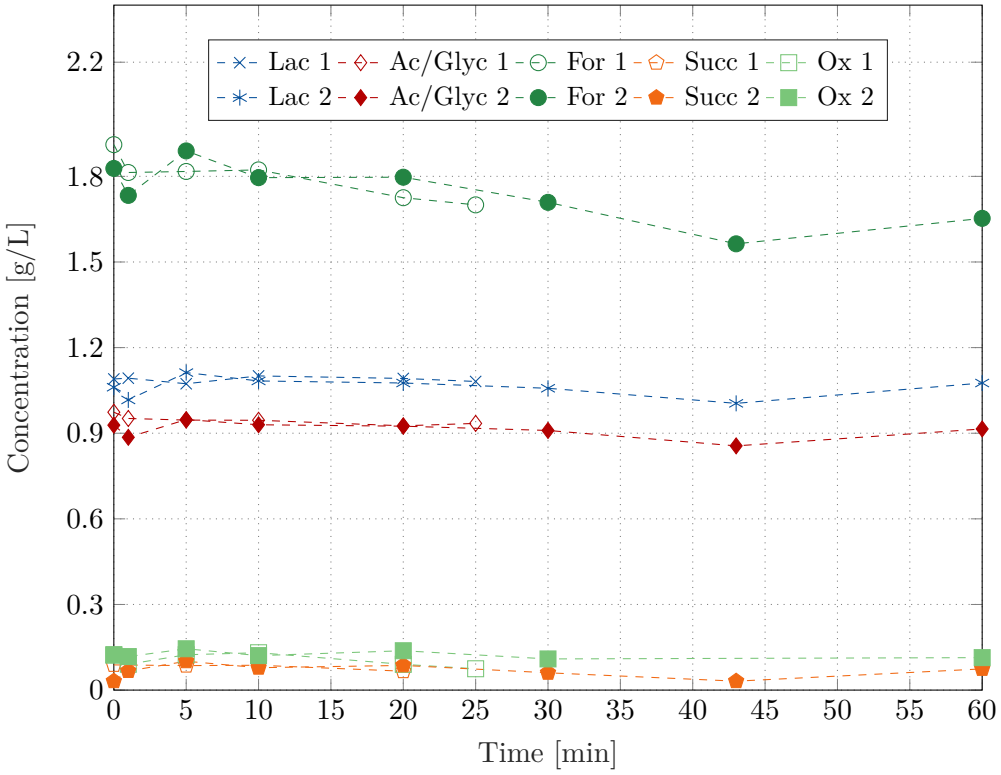

Figure 5.10: Concentration of short organic acid anions in samples withdrawn from the salt compartment during the two electrodialysis experiments with diluted black liquor.

1.55 mg/(L min) of chloride were transported. No explanation could be found for the higher transport rate in the second experiment.

Figure 5.10 shows the concentration of anions present in the feed compartment during the electrodialytic treatment of diluted black liquor. As the samples had to be treated with OnGuard II Ag cartridges prior to analysis, it was not possible to quantify chloride present in the salt compartment. Other than the displayed anions could not be detected.

In the first experiment the initially measured concentrations of lactate, the sum of acetate and glycolate, formate, succinate and oxalate were 1.09 g/L, 0.97 g/L, 1.91 g/L, 0.09 g/L and 0.12 g/L. The respective values for the second experiment were 1.06 g/L, 0.93 g/L, 1.83 g/L, 0.03 g/L and 0.12 g/L.

Concentrations of lactate, acetate/glycolate, succinate and oxalate stayed almost constant over the duration of the two experiments. Minor fluctuations are a result of pipetting errors and other measurement inaccuracies. The fact that almost none of these acid anions is depleted from the salt compartment confirms the low accumulation rates observed in the acid compartment.

Formate depletion of approximately 200 mg/L in the feed fits well to the formate

Table 5.4: Results of the mass balance of short organic acid anions during the two electrodialysis experiments with diluted black liquor. The initially measured concentration was taken as 100 %.

Diluted Black Liquor 1				Diluted Black Liquor 2			
Time [min]	Lactate [%]	Acetate [%]	Formate [%]	Time [min]	Lactate [%]	Acetate [%]	Formate [%]
0	0	0	0	0	0	0	0
1	0.16	−1.67	−4.49	1	−4.20	−4.66	−4.55
5	−1.63	−2.31	−3.33	5	4.84	3.04	5.46
10	0.98	−2.99	−2.09	10	2.07	−0.94	0.60
20	0.22	−4.83	−5.54	20	1.39	−0.71	3.12
25	−0.66	−3.76	−6.22	30	−0.35	−2.05	0.02
				43	−5.32	−5.98	−5.63
				60	1.39	0.35	0.94

concentration detected in the acid compartment. 210.31 mg/L of formate were measured at the end of the second experiment. After subtraction of the initially present concentration of 18.07 mg/L, it was concluded that 192.24 mg/L were recovered from the feed by the electrodialytic treatment. However, 1.7 g/L, referring to 89 % of the initially present formate concentration were still present in the feed solution after the experiment was terminated.

In table 5.4 the results of the mass balances of anions detected in more than one compartment can be seen. The calculation procedure is the same as described above. The errors determined were always lower than 6 %. Small losses can result from pipetting errors and other small measurement inaccuracies. To avoid some mass balance errors in future experiments, the volumes present in the compartments at the end of the experiment need to be determined.

Even though the anion transport from the salt to the acid compartment works, further improvements of the experimental procedure are necessary. One major challenge for the electrodialytic treatment of black liquor is the adsorption of lignin on the ion-exchange membranes. This is most likely the reason for electric power losses over time. Complete removal of lignin prior to electrodialysis is crucial. As discussed in a previous chapter, many authors reported on ultrafiltration to efficiently remove lignin from spent pulping liquor. If the lignin adsorption problem is solved, one may consider to prolong the desalting time of black liquor. However, at this point a longer desalting time does not make sense.

Considering evaluation, the volumes in the compartments at the end of the experiment need to be determined. This would minimize mass balance errors and provide the possibility to comment on water transport as a result of osmosis and hydration shell transport. Additionally, rigorous determination of pH and conductivity has to be performed. Using new electrodes for these purposes has to be considered.

6 Summary and Outlook

In the present work the basics for future research activities dealing with the determination of inorganic and organic compounds of black liquor were created. Additionally, the electrodialytic isolation of organic acids and alkaline cooking chemicals from black liquor was investigated.

The first part of this thesis dealed with the commissioning of a high-pressure anion-exchange chromatography with two different detection systems. HPAEC in its PAD configuration was installed to measure sugars, typically present in wood and process streams of the pulp and paper industry. HPAEC-sCD was set up for the simultaneous separation and determination of organic acid anions and inorganic anions present in black liquor. An instrument method providing the possibility to perform qualitative and quantitative analysis of lactate, acetate, glycolate, formate, chloride, succinate, sulfate, oxalate and phosphate was developed. Additionally, a sample preparation procedure including a solid phase extraction step with Dionex OnGuard II Ag cartridges was set up. This procedure provides the possibility to selectively remove high chloride concentrations. In a recovery experiment it was confirmed that no other anions than chloride are trapped on the OnGuard II Ag cartridge. For both anion chromatography configurations a detailed trouble shooting section is included in this work.

Electrodialysis is a method to recover aliphatic carboxylic acids and hydroxy carboxylic acids from black liquor in their free acid form. Bipolar electrodialysis provides the advantage that organic acid anions and cations from cooking chemicals can be concentrated at the same time, but in different compartments. This makes bipolar electrodialysis especially interesting for treatment of black liquor.

At first, proof of concept experiments were performed using a model solution simulating the properties of black liquor. This solution contained 5 g/L acetate, 5 g/L lactate and 3 g/L formate. The pH was adjusted to approximately 13.5 using solid NaOH pellets. During the experiment the electric power of the apparatus rose until a plateau was reached. This is most likely due to the increasing temperature of the liquid streams. Increasing temperature causes the ions to gain mobility and therefore resistance decreases.

The pH value was determined offline by a pH electrode. Both experiments showed that the pH value in the salt compartment decreases by around 0.25 pH units between the beginning and the end of the experiment. The pH of the base compartment constantly increased by around 0.9 pH units throughout both experiments. The pH of the acid compartment showed greater deviations between the two experiments. During the first experiment a pH drop of 1.1 pH units was observed. However, at the end of the second experiment the pH value was only 0.3 units

smaller than the initial one. Most likely this is caused by the presence of chloride in the feed compartment, resulting from HCl used for pH adjustment. Chloride is transported to the acid compartment where hydrochloric acid is formed. In the second experiment no HCl was used to adjust the feed pH and therefore no chloride can be transported to the acid compartment. This observation was confirmed by IC analysis. Chloride depletion of 3.08 g/L was detected in the feed compartment of the first experiment. However, in the feed of the second experiment no chloride could be found. Also formate, acetate and lactate concentrations decreased in the feed compartment. Cross-checking the acid compartment resulted in an increase of formate, acetate and lactate concentrations. Among the organic acid anions the highest accumulation rate was observed for formate with 1.28 g/L in the first experiment and 1.25 g/L in the second one.

The last part of this thesis focused on the electrodialytic treatment of diluted black liquor. Dilution with deionized water was necessary as the used black liquor showed a total dry substance content of 41.6 %. To reduce the risk of membrane fouling a total dry substance content of 5 % was chosen. The electric power was observed to decrease during the whole experiment. This indicates an increasing resistance against ion transport, which might result from membrane fouling by lignin adsorption. The temperature increase of the liquid streams could not counteract this effect.

pH values of acid and base compartment samples confirmed that acidic or alkaline compounds are accumulated. The pH of the diluted black liquor does not change throughout both experiments. This is most likely caused by the buffering effect of lignin. Results from the ion chromatographic analysis of samples withdrawn from the acid compartment showed the highest accumulation rates for formate (3.66 mg/(L min) in the first experiment and 3.20 mg/(L min) in the second experiment. During the second experiment also chloride could be detected. Lactate was found only during the first experiment. Additionally, the increase in lactate concentration over time was extremely low with 1.55 mg/L within 25 min. This refers to an accumulation rate of 0.06 mg/(L min). Similar behavior was observed for acetate. Maybe these two anions are more prone to adsorption onto the lignin deposition layer formed on the surface of the ion-exchange membranes. None of the anions determined in the feed compartment showed significant depletion over time. Only the formate concentration decreased by around 200 mg/L. However, the current decreased from 0.8 A to 0.25 A over the desalting time of 60 min, most likely due to fouling. Therefore, running the experiment for longer time to accumulate more formate within the acid compartment is not possible. Lignin removal from the feed stream for example by ultrafiltration prior to electrodialysis needs to be considered. This would prevent fouling a priori.

Additionally, in all further electrodialytic experiments the volumes of the single streams should be determined at the end of the experiment. This would minimize the mass balance error, as volume transfer caused by osmosis and volume shift as a result of the hydration shell transfer would be accounted for.

In the present work all requirements to perform more detailed analysis on the iso-

lation behavior of organic acids and recovery of cooking chemicals from black liquor were established. A pilot-scale electrodialysis apparatus in the bipolar configuration was set up, as well as the analytical basis for ion chromatographic resolution of multiple inorganic and organic acid anions was accomplished. Critical steps were identified and discussed for both applications.

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List of Abbreviations

AEM	anion-exchange membrane
BPM	bipolar membrane
CEM	cation-exchange membrane
CR-ATC	continuously regenerated anion trap column
DHPA	2,5-dihydroxypentanoic acid
ESI-MS	electrospray ionization mass spectrometry
GISA	glucoisosaccarinic acid
HBA	2-hydroxybutanoic acid
HPAEC	high-pressure anion-exchange chromatography
HPIC	high-pressure ion chromatography
HPLC	high-pressure/performance liquid chromatography
IC	ion chromatography
IPAD	integrated pulsed amperometric detection
LOD	limit of detection
LOQ	limit of quantification
PEEK	polyether ether ketone
PTFE	polytetrafluorethylene
PAD	pulsed amperometric detection
sCD	suppressed conductivity detection
SPE	solid phase extraction
TOC	total organic carbon
XISA	xyloisosaccarinic acid

List of Symbols

A	peak dispersion term due to eddy diffusion	[m]
$A_{\mathbf{s}}$	asymmetry factor	
a	half peak height (leading side)	[s]
B	longitudinal diffusion term	[s^{-1}]
b	half peak height (tailing side)	[s]
C	lateral diffusion term	[s]
$C_{\mathbf{elec}}$	electrical conductance	[S]
c	concentration	[$mol\,m^{-3}$]
D	diffusion coefficient	[$m^2\,s^{-1}$]
ϵ	dielectric constant	[$C^2\,m^{-2}\,N^{-1}$]
F	Faraday constant	[$A\,s\,mol^{-1}$]
$F_{\mathbf{C}}$	Coulomb force	[N]
G	Gibbs free energy	[$kg\,m^2\,s^{-2}$]
H	enthalpy	[$kg\,m^2\,s^{-2}$]
$H_{\mathbf{theor}}$	height of a theoretical stage	[m]
h	peak height	
I	current	[A]
$K_{\mathbf{cell}}$	cell constant	[m^{-1}]
κ	specific conductivity	[$S\,m^{-1}$]
L	column length	[m]
$\Lambda_{\mathbf{m}}$	molar conductivity	[$S\,m^2\,mol^{-1}$]
N	number of stages	
n	molar flow density	[$mol\,s^{-1}\,m^{-2}$]

ν	flow velocity	$[\mathrm{m\,s^{-1}}]$
P	electric power	[W]
ϕ	electric potential	[V]
q	charge	[C]
R	gas constant	$[\mathrm{J\,mol^{-1}\,K^{-1}}]$
$R_\mathbf{s}$	resolution	
r	distance between two ions	[m]
σ	standard deviation	
T	temperature	[K]
t	time	[s]
$t_\mathbf{m}$	column dead time	[s]
$t_\mathbf{ms}$	gross retention time	[s]
$t_\mathbf{s}$	solute retention time	[s]
$w_\mathbf{b}$	peak width at the base	[s]
$w_\mathbf{h}$	peak width at half the peak height	[s]
V	voltage	[V]
$\dot{V}$	volume stream	$[\mathrm{m^3\,s^{-1}}]$
z	charge number	

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Appendix

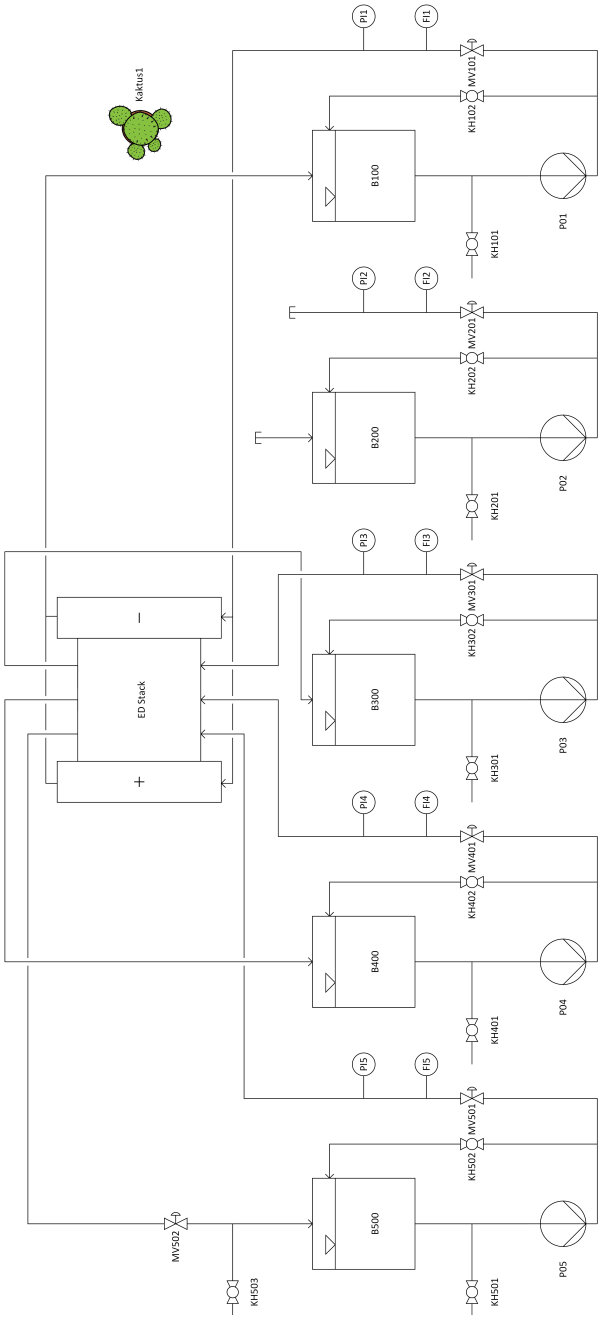

Figure 6.1: Flow diagram of the electrodialysis apparatus in bipolar configuration.

Certificate of Analysis

1000 PPM Carbonate IC Standard

Certified Reference Material

Product ID ICS034-100ML
Lot LRAB6174
Expiration Date December 31, 2020
Storage Conditions Store at room temperature.

Analyte	*Units*	*Certified Value* [1,4]	***k*** [5]
Carbonate	ug/mL	1000 ± 17.9	2.00

Sample Information

ADDITIONAL INFORMATION
The sample is ready to use.
No sample preparation is required.

1 Certified value - based on the robust mean of round robin, interlaboratory study and analytically verified by RTC with associated uncertainties from the preparation and analytical procedures.
4 Ucrm - Uncertainty values in this document are expressed as Expanded Uncertainty (Ucrm) corresponding to the 95% confidence interval. Ucrm is derived from the combined standard uncertainty multiplied by the coverage factor k, which is obtained from a *t*-distribution and degrees of freedom. The components of combined standard uncertainty include the uncertainties due to characterization, homogeneity, long term stability, and short term stability (transport). The components due to stability are generally considered to be negligible unless otherwise indicated by stability studies. The mathematical representation of the Ucrm calculation is as follows:

$$u_{CRM} = \sqrt{u_{char}^2 + u_{hom\ ogeneity}^2 + u_{stability}^2}$$

5 ***k*:** Coverage factor derived from a t-distribution table, based on the degrees of freedom of the data set. **Confidence interval = 95%**

Traceability: The standard was manufactured under an ISO/IEC 17025:2005 certified quality system. The balance used to weigh raw materials is accurate to +/- 0.0001g and calibrated regularly using mass standards traceable to NIST. All dilutions were preformed gravimetrically. Additionally, individual analytes are traceable to NIST SRMs where available and specified above.

Homogeneity: Homogeneity was assessed in accordance with ISO Guide 35. Completed units were sampled using a random stratified sampling protocol. The results of chemical analysis were then compared using a one-way analysis of variance approach as described by TNI EL-V3-2009 Appendix A.2. See Instructions for minimum sub-sample size.

THIS PRODUCT WAS DESIGNED, PRODUCED AND VERIFIED FOR ACCURACY AND STABILITY IN ACCORDANCE WITH ISO/IEC 17025:2005 (ANAB Cert AT-1467) and ISO GUIDE 34:2009 (ANAB Cert AR-1470).

MSDS reports for components comprising greater than 1.0% of the solution or 0.1% for components known to be carcinogens are available upon request.

Robert O'Brien - QC Supervisor

Mark Pooler - QA Supervisor

Certification Date September 29, 2017
Version 5104-9292017

ANAB ACCREDITED ISO GUIDE 34 REFERENCE MATERIAL PRODUCER

ANAB ACCREDITED ISO/IEC 17025 TESTING LABORATORY

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TraceCERT®
Traceable Certified Reference Materials

SIGMA-ALDRICH®

Certificate

Produced in double accredited laboratory fulfilling ISO/IEC 17025 and ISO 17034

This certificate is designed in accordance with ISO Guide 31 [1].

Object of certification:	**Acetate Standard for IC**
Product no.:	**51791**
Lot no.	**BCBV8223**
Composition:	Acetic acid (high purity quality) and sodium hydroxide solution suitable for trace analysis in high-purity water (18.2 MΩ·cm, 0.22 µm filtered). The bottled solution is stabilized with sodium azide (about 5 mg/L) and additionally filtered through a 0.2 µm membrane.
Intended use:	Calibration of ion chromatography or any other analytical technique.
Storing and handling:	This reference material shall be stored between 5 °C and 30 °C whereas the certified value is guaranteed when the long-term storage temperature will not exceed 25°C. Before every use of the material the bottle must be shaken well and its temperature has to be 20°C. If storage of a partially used bottle is necessary, the cap should be tightly sealed and the bottle should be stored at reduced temperature (e.g. refrigerator) to minimize transpiration rate.
Expiry date:	**AUG 2020**
Certificate issue date:	20 FEB 2018
Certificate version:	01
Bottle opening date:	_____

The certified values and uncertainties are according to ISO Guide 35 [2] and Eurachem/CITAC Guide [3]

Constituent	Certified value at 20°C and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]	
Acetate	**1'001 mg kg^{-1} ± 4 mg kg^{-1}**	**1'000 mg L^{-1} ± 4 mg L^{-1}**
Traceability [4]	NIST SRM 84I, Potassium Hydrogen Phthalate	

Measurand	Certified value and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]
Density at 20°C	**0.999 g mL^{-1} ± 0.0005 g mL^{-1}**

CRM operations: S.Matt
S.Matt

Approving Officer:
P. Zell, Ph.D.

ISO 17034	ISO/IEC 17025	ISO 9001
SRMS 0001	STS 0490	005356 QM08

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1. Concept of Certification

The certified concentrations and expanded uncertainties of the analyte are based on the results obtained from gravimetrical production and from the analytical results determined using acid-base titration.

Gravimetric preparation using well defined and pure materials is a practical realization of concentration units, through conversion of mass to amount of substance [4]. All high-precision balances are periodically calibrated by a third party and certified according to DAkkS guidelines (DAkkS = Deutsche Akkreditierungsstelle GmbH, which is the national accreditation body for the Federal Republic of Germany).

Production and certification of this CRM are performed under double-accreditation in accordance with ISO/IEC 17025 [5] and also ISO 17034 [6]. Storage stability, leaching and homogeneity tests are also considered for certification.

2. Starting Material Content by Titration

The content of the starting material (acetic acid, P/N 33209, Lot SZBB2210V) is performed by volumetric acid-base titrations with carbonate free 1 mol/L NaOH-solution using a combined pH-electrode.

Seven starting material samples and seven reference material samples are prepared separately and then titrated in one set. All results are traced gravimetrically to National Bureau of Standards (NIST) Standard Reference Material 84l acidimetric standard, potassium hydrogen phthalate (99.9934%).

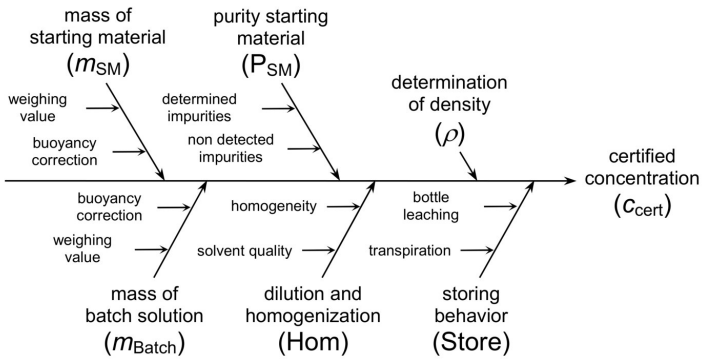
Content of starting material: 99.81 %
Expanded uncertainty (k=2): 0.14 %

3. Density Measurement

The density measurement is carried out according to ISO 15212-1 [7] and using the digital density meter DMA 4500M from Anton Paar with an oscillating U-tube installed. The measurement uncertainty is calculated according to Eurachem/CITAC Guide and reported as combined expanded uncertainty at the 95% confidence level.

4. Uncertainty Evaluation

All uncertainties are calculated according to Eurachem/CITAC Guide [3] and reported as combined expanded uncertainties at the 95% confidence level. For gravimetric preparation the uncertainty contributions are illustrated by the following cause-effect diagram [8]:



Typical contributions:

$u(m_{SM})$	< 0.01%
$u(m_{Batch})$	< 0.01%
$u(P_{SM})$	< 0.10%
u(Hom)	< 0.03%
u(Store)	< 0.20%
$u(\rho)$	< 0.05%

Combined uncertainty [9]:

$u_c(c_{cert})$ < 0.2%

Expanded uncertainty:

$\boldsymbol{U(c_{cert})}$ < **0.4%**

References

[1] ISO Guide 31:2015, “Reference materials - Contents of certificates, labels and accompanying documentation”
[2] ISO Guide 35:2017, “Reference materials – Guidance for characterization and assessment of homogeneity and stability”
[3] Eurachem/CITAC Guide, 3rd Ed. (2012), “Quantifying uncertainty in analytical measurement”
[4] Eurachem/CITAC Guide, 1st Ed. (2003) “Traceability in chemical measurement”
[5] ISO/IEC 17025:2005, “General requirements for the competence of testing and calibration laboratories”
[6] ISO 17034:2016, “General requirements for the competence of reference material producers”
[7] DIN EN ISO 15212-1:1998, Oscillation-type density meters - Part 1: Laboratory instruments
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[9] Calculated by combination of the squared contribution values

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Certificate

Produced in double accredited laboratory fulfilling ISO/IEC 17025 and ISO Guide 34

This certificate is designed in accordance with ISO Guide 31 [1].

Object of certification:	**Glycolate standard for IC**
Product no.:	**07391**
Lot no.	**BCBS2142V**
Composition:	Glycolic acid (high purity quality) in high-purity water (18.2 MΩ·cm, 0.22 µm filtered). The bottled solution is stabilized with sodium azide (about 5 mg/L) and additionally filtered through a 0.2 µm membrane.
Intended use:	Calibration of ion chromatography or any other analytical technique.
Storing and handling:	This reference material shall be stored between 5 °C and 30 °C whereas the certified value is guaranteed when the long-term storage temperature will not exceed 25°C. Before every use of the material the bottle must be shaken well and its temperature has to be 20°C. If storage of a partially used bottle is necessary, the cap should be tightly sealed and the bottle should be stored at reduced temperature (e.g. refrigerator) to minimize transpiration rate.
Expiry date:	**JUN 2019**
Certificate issue date:	16 SEP 2016
Bottle opening date:	

The certified values and uncertainties are according to ISO Guide 35 [2] and Eurachem/CITAC Guide [3]

Constituent	Certified value at 20°C and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]	
Glycolate	**1'001 mg kg^{-1} ± 5 mg kg^{-1}**	**1'000 mg L^{-1} ± 5 mg L^{-1}**
Traceability [4]	NIST SRM 84I, Potassium Hydrogen Phthalate	

Measurand	Certified value and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]
Density at 20°C	**0.9986 g mL^{-1} ± 0.0005 g mL^{-1}**

CRM operations: S.Matt
S.Matt

Certification body:
K.-D. Schmidt, Ph.D.

ISO Guide 34 ISO/IEC 17025 ISO 9001

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1. CONCEPT OF CERTIFICATION

The certified concentrations and expanded uncertainties of the analyte are based on the results obtained from gravimetrical production and from the analytical results determined using high-resolution quantitative NMR, which is recognized as primary measurement method.

Gravimetric preparation using well defined and pure materials is a practical realization of concentration units, through conversion of mass to amount of substance [4]. All high-precision balances are periodically calibrated by a third party and certified according to DAkkS guidelines (DAkkS = Deutsche Akkreditierungsstelle GmbH, which is the national accreditation body for the Federal Republic of Germany).

Production and certification of this CRM are performed under double-accreditation in accordance with ISO/IEC 17025 [5] and also ISO Guide 34 [6]. Storage stability, leaching and homogeneity tests are also considered for certification.

2. STARTING MATERIAL CONTENT BY qNMR

The absolute content of starting material is measured by high-resolution quantitative NMR measurements on a Bruker 600 MHz Avance III NMR spectrometer.

The certification of the content is performed using 5-10 separate samples which are each spiked with an adequate amount of internal reference and then immediately dissolved in deuterated solvent. In most cases 16-32 scans are recorded for every sample with a ^{1}H relaxation time of d1 = 60 seconds. Quantification of the content is directly calculated from the ^{1}H-NMR peak areas and the initial weights of the sample and reference substance. After Analysis of variance (ANOVA) the resulting standard deviation is included into the uncertainty calculation of the certified value.

Extensive stability and homogeneity tests are considered for certification.

Accelerated stability test is performed with samples which are stored above the recommended storing temperature (mostly at 45 °C) and qNMR double determinations after 1, 3, 9 and 18 months.

Long term stability test is performed with samples which are stored at the recommended storing temperature and qNMR double determination after 24 and 48 months.

Homogeneity of the material is tested by qNMR measurements using 5-10 subsamples which are taken from different positions in the entire bulk material. The recommended minimal sample size is taken for all the homogeneity test samples. ANOVA results are included into the calculation of content uncertainty of this CRM.

Starting material	Starting material content with expanded uncertainty	Traceable to
Glycolic acid P/N 94815 Lot BCBQ4069V	**99.8 % ± 0.2 %**	NIST SRM 84l,potassium hydrogen phthalate

3. DENSITY MEASUREMENT

The density measurement is carried out according to ISO 15212-1 [7] and using the digital density meter DMA 4500M from Anton Paar with an oscillating U-tube installed. The measurement uncertainty is calculated according to Eurachem/CITAC Guide and reported as combined expanded uncertainty at the 95% confidence level.

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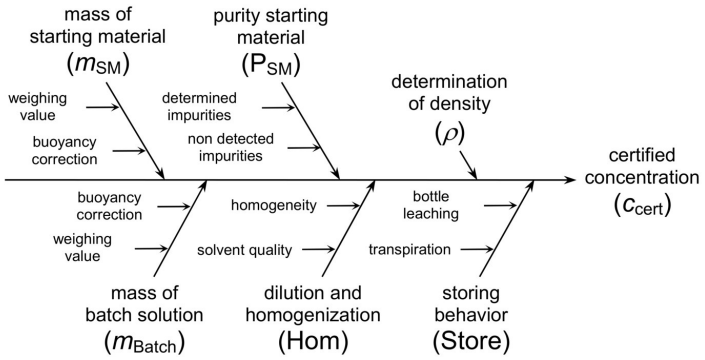
4. UNCERTAINTY EVALUATION

All uncertainties are calculated according to Eurachem/CITAC Guide [3] and reported as combined expanded uncertainties at the 95% confidence level. For gravimetric preparation the uncertainty contributions are illustrated by the following cause-effect diagram [8]:



Typical contributions:

$u(m_{SM})$	< 0.01%
$u(m_{Batch})$	< 0.01%
$u(P_{SM})$	< 0.1%
u(Hom)	< 0.03%
u(Store)	< 0.20%
$u(\rho)$	< 0.05%

Combined uncertainty [9]:

$u_c(c_{cert})$	< 0.2%

Expanded uncertainty:

$\boldsymbol{U(c_{cert})}$	**< 0.5%**

References

[1] ISO Guide 31:2000, “Reference materials - Contents of certificates and labels”
[2] ISO Guide 35:2006, “Reference materials - General and statistical principles for certification”
[3] Eurachem/CITAC Guide, 3rd Ed. (2012), “Quantifying uncertainty in analytical measurement”
[4] Eurachem/CITAC Guide, 1st Ed. (2003) “Traceability in chemical measurement”
[5] ISO/IEC 17025, 2nd Ed. (2005), “General requirements for the competence of testing and calibration laboratories”
[6] ISO Guide 34:2009, “General requirements for the competence of reference material producers”
[7] DIN EN ISO 15212-1:1998, Oscillation-type density meters - Part 1: Laboratory instruments
[8] Reichmuth, A., Wunderli, S., Weber, M., Meyer, V. R. (2004), “The uncertainty of weighing data obtained with electronic analytical balances”, Microchimica Acta 148: 133-141.
[9] Calculated by combination of the squared contribution values

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TraceCERT®
Traceable Certified Reference Materials

SIGMA-ALDRICH®

Certificate

Produced in double accredited laboratory fulfilling ISO/IEC 17025 and ISO 17034

This certificate is designed in accordance with ISO Guide 31 [1].

Object of certification:	**Lactate standard for IC**
Product no.:	**07096**
Lot no.	**BCBV6554**
Composition:	Magnesium L-lactate hydrate (high purity quality) in high-purity water (18.2 MΩ·cm, 0.22 µm filtered). The bottled solution is stabilized with sodium azide (about 5 mg/L) and additionally filtered through a 0.2 µm membrane.
Intended use:	Calibration of ion chromatography or any other analytical technique.
Storing and handling:	This reference material shall be stored between 5 °C and 30 °C whereas the certified value is guaranteed when the long-term storage temperature will not exceed 25°C. Before every use of the material the bottle must be shaken well and its temperature has to be 20°C. If storage of a partially used bottle is necessary, the cap should be tightly sealed and the bottle should be stored at reduced temperature (e.g. refrigerator) to minimize transpiration rate.
Expiry date:	**JUL 2020**
Certificate issue date:	26 JAN 2018
Certificate version:	01
Bottle opening date:	

The certified values and uncertainties are according to ISO Guide 35 [2] and Eurachem/CITAC Guide [3]

Constituent	Certified value at 20°C and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]	
Lactate	**1'002 mg kg^{-1} ± 5 mg kg^{-1}**	**1'001 mg L^{-1} ± 5 mg L^{-1}**
Traceability [4]	NIST SRM 84l, Potassium Hydrogen Phthalate and NIST SRM 350b, Benzoic Acid	

Measurand	Certified value and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]
Density at 20°C	**0.9989 g mL^{-1} ± 0.0005 g mL^{-1}**

CRM operations: S.Matt
S.Matt

Approving Officer: C. Geitner
C. Geitner, Ph.D.

SWISS ACCREDITATION sas.admin.ch SRMS 0001 — **ISO 17034** SRMS 0001

SWISS ACCREDITATION sas.admin.ch STS 0490 — **ISO/IEC 17025** STS 0490

Certified QRP Management System — **ISO 9001** 005356 QM08

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SIGMA-ALDRICH®

1. CONCEPT OF CERTIFICATION

The certified concentrations and expanded uncertainties of the analyte are based on the results obtained from gravimetrical production and from the analytical results determined using high-resolution quantitative NMR, which is recognized as primary measurement method.

Gravimetric preparation using well defined and pure materials is a practical realization of concentration units, through conversion of mass to amount of substance [4]. All high-precision balances are periodically calibrated by a third party and certified according to DAkkS guidelines (DAkkS = Deutsche Akkreditierungsstelle GmbH, which is the national accreditation body for the Federal Republic of Germany).

Production and certification of this CRM are performed under double-accreditation in accordance with ISO/IEC 17025 [5] and also ISO 17034 [6]. Storage stability, leaching and homogeneity tests are also considered for certification.

2. STARTING MATERIAL CONTENT BY qNMR

The absolute content of starting material is measured by high-resolution quantitative NMR measurements on a Bruker 600 MHz Avance III NMR spectrometer.

The certification of the content is performed using 5-10 separate samples which are each spiked with an adequate amount of internal reference and then immediately dissolved in deuterated solvent. In most cases 16-32 scans are recorded for every sample with a ^{1}H relaxation time of d1 = 60 seconds. Quantification of the content is directly calculated from the ^{1}H-NMR peak areas and the initial weights of the sample and reference substance. After Analysis of variance (ANOVA) the resulting standard deviation is included into the uncertainty calculation of the certified value.

Extensive stability and homogeneity tests are considered for certification.

Accelerated stability test is performed with samples which are stored above the recommended storing temperature (mostly at 45 °C) and qNMR double determinations after 1, 3, 9 and 18 months.

Long term stability test is performed with samples which are stored at the recommended storing temperature and qNMR double determination after 24 and 48 months.

Homogeneity of the material is tested by qNMR measurements using 5-10 subsamples which are taken from different positions in the entire bulk material. The recommended minimal sample size is taken for all the homogeneity test samples. ANOVA results are included into the calculation of content uncertainty of this CRM.

Starting material	Starting material content with expanded uncertainty	Traceable to
Magnesium L-lactate hydrat P/N 40394 Lot BCBR1672V	**74.1 % ± 0.2 %**	NIST SRM 84l,potassium hydrogen phthalate and NIST SRM 350b, benzoic acid

3. DENSITY MEASUREMENT

The density measurement is carried out according to ISO 15212-1 [7] and using the digital density meter DMA 4500M from Anton Paar with an oscillating U-tube installed. The measurement uncertainty is calculated according to Eurachem/CITAC Guide and reported as combined expanded uncertainty at the 95% confidence level.

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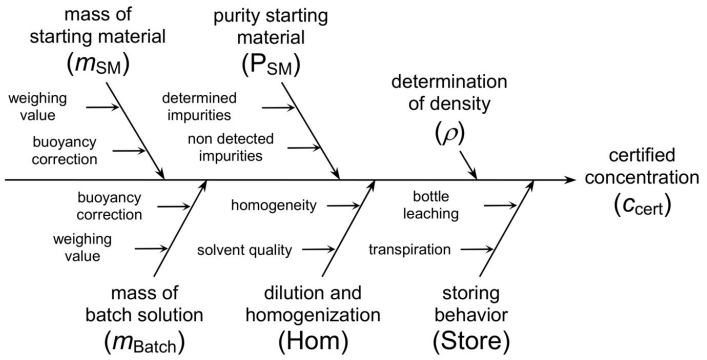
4. UNCERTAINTY EVALUATION

All uncertainties are calculated according to Eurachem/CITAC Guide [3] and reported as combined expanded uncertainties at the 95% confidence level. For gravimetric preparation the uncertainty contributions are illustrated by the following cause-effect diagram [8]:



Typical contributions:

$u(m_{SM})$	< 0.01%
$u(m_{Batch})$	< 0.01%
$u(P_{SM})$	< 0.1%
u(Hom)	< 0.03%
u(Store)	< 0.20%
$u(\rho)$	< 0.05%

Combined uncertainty [9]:

$u_c(c_{cert})$	< 0.3%

Expanded uncertainty:

$\boldsymbol{U(c_{cert})}$	**< 0.6%**

References

[1] ISO Guide 31:2015, “Reference materials - Contents of certificates, labels and accompanying documentation”
[2] ISO Guide 35:2017, “Reference materials – Guidance for characterization and assessment of homogeneity and stability”
[3] Eurachem/CITAC Guide, 3rd Ed. (2012), “Quantifying uncertainty in analytical measurement”
[4] Eurachem/CITAC Guide, 1st Ed. (2003) “Traceability in chemical measurement”
[5] ISO/IEC 17025:2005, “General requirements for the competence of testing and calibration laboratories”
[6] ISO 17034:2016, “General requirements for the competence of reference material producers”
[7] DIN EN ISO 15212-1:1998, Oscillation-type density meters - Part 1: Laboratory instruments
[8] Reichmuth, A., Wunderli, S., Weber, M., Meyer, V. R. (2004), “The uncertainty of weighing data obtained with electronic analytical balances”, Microchimica Acta 148: 133-141.
[9] Calculated by combination of the squared contribution values

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SIGMA-ALDRICH®

Certificate

Produced in double accredited laboratory fulfilling ISO/IEC 17025 and ISO Guide 34

This certificate is designed in accordance with ISO Guide 31 [1].

Object of certification:	**Oxalate standard for IC**
Product no.:	**73139**
Lot no.	**BCBS3060V**
Composition:	Sodium oxalate (high purity quality) in high-purity water (18.2 MΩ·cm, 0.22 µm filtered). The bottled solution is stabilized with sodium azide (about 5 mg/L) and additionally filtered through a 0.2 µm membrane.
Intended use:	Calibration of ion chromatography or any other analytical technique.
Storing and handling:	This reference material shall be stored between 5 °C and 30 °C. Before every use of the material the bottle must be shaken well and its temperature has to be 20°C. If storage of a partially used bottle is necessary, the cap should be tightly sealed and the bottle should be stored at reduced temperature (e.g. refrigerator) to minimize transpiration rate.
Expiry date:	**OCT 2019**
Certificate issue date:	13 DEC 2016
Bottle opening date:	

The certified values and uncertainties are according to ISO Guide 35 [2] and Eurachem/CITAC Guide [3]

Constituent	Certified value at 20°C and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]	
Oxalate	**1'001 mg kg^{-1} ± 4 mg kg^{-1}**	**1'000 mg L^{-1} ± 4 mg L^{-1}**
Traceability [4]	NIST SRM 8040, sodium oxalate	

Measurand	Certified value and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]
Density at 20°C	**0.9995 g mL^{-1} ± 0.0005 g mL^{-1}**

CRM operations: S.Matt
S.Matt

Certification body:
K.-D. Schmidt, Ph.D.

ISO Guide 34 ISO/IEC 17025 ISO 9001

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SIGMA-ALDRICH®

1. Concept of Certification

The certified concentrations and expanded uncertainties of the analyte are based on the results obtained from gravimetrical production and from the analytical results determined using acid-base titration.

Gravimetric preparation using well defined and pure materials is a practical realization of concentration units, through conversion of mass to amount of substance [4]. All high-precision balances are periodically calibrated by a third party and certified according to DAkkS guidelines (DAkkS = Deutsche Akkreditierungsstelle GmbH, which is the national accreditation body for the Federal Republic of Germany).

Production and certification of this CRM are performed under double-accreditation in accordance with ISO/IEC 17025 [5] and also ISO Guide 34 [6]. Storage stability, leaching and homogeneity tests are also considered for certification.

2. Starting Material Content by Titration

The content of the starting material was measured by volumetric redox titrations with 0.2 mol/l $KMnO_4$-solution using a Pt-Titrode electrode.

Twenty starting material samples (P/N 71804, Lot BCBR5525V) and eight reference material samples (dried at 105°C for 3 hours) were prepared separately and then titrated in one set. All the measurements are traced gravimetrically to National Institute of Standards and Technology (NIST) Standard Reference Material 8040 sodium oxalate (99.951%, dried at 105°C for 3 hours).

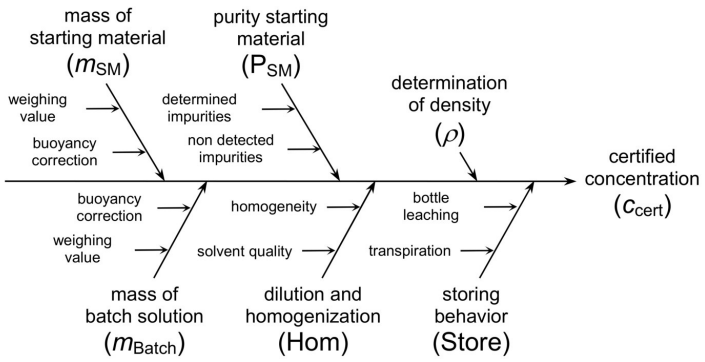
Content of starting material: 99.86 %
Expanded uncertainty (k=2): 0.09 %

3. Density Measurement

The density measurement is carried out according to ISO 15212-1 [7] and using the digital density meter DMA 4500M from Anton Paar with an oscillating U-tube installed. The measurement uncertainty is calculated according to Eurachem/CITAC Guide and reported as combined expanded uncertainty at the 95% confidence level.

4. Uncertainty Evaluation

All uncertainties are calculated according to Eurachem/CITAC Guide [3] and reported as combined expanded uncertainties at the 95% confidence level. For gravimetric preparation the uncertainty contributions are illustrated by the following cause-effect diagram [8]:



Typical contributions:

$u(m_{SM})$	< 0.01%
$u(m_{Batch})$	< 0.01%
$u(P_{SM})$	< 0.05%
u(Hom)	< 0.03%
u(Store)	< 0.20%
$u(\rho)$	< 0.05%

Combined uncertainty [9]:

$u_c(c_{cert})$ < 0.2%

Expanded uncertainty:

$\boldsymbol{U(c_{cert})}$ **< 0.4%**

References

[1] ISO Guide 31:2000, “Reference materials - Contents of certificates and labels”
[2] ISO Guide 35:2006, “Reference materials - General and statistical principles for certification”
[3] Eurachem/CITAC Guide, 3rd Ed. (2012), “Quantifying uncertainty in analytical measurement”
[4] Eurachem/CITAC Guide, 1st Ed. (2003) “Traceability in chemical measurement”
[5] ISO/IEC 17025, 2nd Ed. (2005), “General requirements for the competence of testing and calibration laboratories”
[6] ISO Guide 34:2009, “General requirements for the competence of reference material producers”
[7] DIN EN ISO 15212-1:1998, Oscillation-type density meters - Part 1: Laboratory instruments
[8] Reichmuth, A., Wunderli, S., Weber, M., Meyer, V. R. (2004), “The uncertainty of weighing data obtained with electronic analytical balances”, Microchimica Acta 148: 133-141.
[9] Calculated by combination of the squared contribution values

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Certificate

Produced in double accredited laboratory fulfilling ISO/IEC 17025 and ISO Guide 34

This certificate is designed in accordance with ISO Guide 31 [1].

Object of certification:	**Succinate standard for IC**
Product no.:	**43057**
Lot no.	**BCBT9110**
Composition:	Succinic acid (high purity quality) in high-purity water (18.2 MΩ·cm, 0.22 µm filtered). The bottled solution is stabilized with sodium azide (about 5 mg/L) and additionally filtered through a 0.2 µm membrane.
Intended use:	Calibration of ion chromatography or any other analytical technique.
Storing and handling:	This reference material shall be stored between 5 °C and 30 °C whereas the certified value is guaranteed when the long-term storage temperature will not exceed 25°C. Before every use of the material the bottle must be shaken well and its temperature has to be 20°C. If storage of a partially used bottle is necessary, the cap should be tightly sealed and the bottle should be stored at reduced temperature (e.g. refrigerator) to minimize transpiration rate.
Expiry date:	**FEB 2020**
Certificate issue date:	19 APR 2017
Certificate version:	01
Bottle opening date:	

The certified values and uncertainties are according to ISO Guide 35 [2] and Eurachem/CITAC Guide [3]

Constituent	Certified value at 20°C and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]	
Succinate	**1'001 mg kg^{-1} ± 4 mg kg^{-1}**	**1'000 mg L^{-1} ± 4 mg L^{-1}**
Traceability [4]	NIST SRM 84I, Potassium Hydrogen Phthalate	

Measurand	Certified value and expanded uncertainty [$U = k \cdot u_c$; $k = 2$]
Density at 20°C	**0.9985 g mL^{-1} ± 0.0005 g mL^{-1}**

CRM operations: S.Matt
S.Matt

Certification body: K.-D. Schmidt, Ph.D.

ISO Guide 34	ISO/IEC 17025	ISO 9001
SRMS 0001	STS 0490	005356 QM08

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SIGMA-ALDRICH®

1. CONCEPT OF CERTIFICATION

The certified concentrations and expanded uncertainties of the analyte are based on the results obtained from gravimetrical production and from the analytical results determined using high-resolution quantitative NMR, which is recognized as primary measurement method.

Gravimetric preparation using well defined and pure materials is a practical realization of concentration units, through conversion of mass to amount of substance [4]. All high-precision balances are periodically calibrated by a third party and certified according to DAkkS guidelines (DAkkS = Deutsche Akkreditierungsstelle GmbH, which is the national accreditation body for the Federal Republic of Germany).

Production and certification of this CRM are performed under double-accreditation in accordance with ISO/IEC 17025 [5] and also ISO Guide 34 [6]. Storage stability, leaching and homogeneity tests are also considered for certification.

2. STARTING MATERIAL CONTENT BY qNMR

The absolute content of starting material is measured by high-resolution quantitative NMR measurements on a Bruker 600 MHz Avance III NMR spectrometer.

The certification of the content is performed using 5-10 separate samples which are each spiked with an adequate amount of internal reference and then immediately dissolved in deuterated solvent. In most cases 16-32 scans are recorded for every sample with a ^{1}H relaxation time of d1 = 60 seconds. Quantification of the content is directly calculated from the ^{1}H-NMR peak areas and the initial weights of the sample and reference substance. After Analysis of variance (ANOVA) the resulting standard deviation is included into the uncertainty calculation of the certified value.

Extensive stability and homogeneity tests are considered for certification.

Accelerated stability test is performed with samples which are stored above the recommended storing temperature (mostly at 45 °C) and qNMR double determinations after 1, 3, 9 and 18 months.

Long term stability test is performed with samples which are stored at the recommended storing temperature and qNMR double determination after 24 and 48 months.

Homogeneity of the material is tested by qNMR measurements using 5-10 subsamples which are taken from different positions in the entire bulk material. The recommended minimal sample size is taken for all the homogeneity test samples. ANOVA results are included into the calculation of content uncertainty of this CRM.

Starting material	Starting material content with expanded uncertainty	Traceable to
Succinic acid P/N 49893 Lot BCBM0043V	**99.5 % ± 0.1 %**	NIST SRM 84l,potassium hydrogen phthalate

3. DENSITY MEASUREMENT

The density measurement is carried out according to ISO 15212-1 [7] and using the digital density meter DMA 4500M from Anton Paar with an oscillating U-tube installed. The measurement uncertainty is calculated according to Eurachem/CITAC Guide and reported as combined expanded uncertainty at the 95% confidence level.

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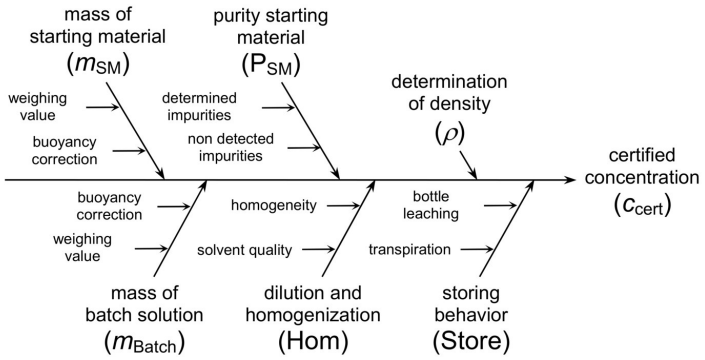
All uncertainties are calculated according to Eurachem/CITAC Guide [3] and reported as combined expanded uncertainties at the 95% confidence level. For gravimetric preparation the uncertainty contributions are illustrated by the following cause-effect diagram [8]:



Typical contributions:

$u(m_{SM})$	< 0.01%
$u(m_{Batch})$	< 0.01%
$u(P_{SM})$	< 0.05%
u(Hom)	< 0.03%
u(Store)	< 0.20%
$u(\rho)$	< 0.05%

Combined uncertainty [9]:

$u_c(c_{cert})$ < 0.2%

Expanded uncertainty:

$U(c_{cert})$ < 0.4%

References

[1] ISO Guide 31:2015, “Reference materials - Contents of certificates, labels and accompanying documentation”
[2] ISO Guide 35:2006, “Reference materials - General and statistical principles for certification”
[3] Eurachem/CITAC Guide, 3rd Ed. (2012), “Quantifying uncertainty in analytical measurement”
[4] Eurachem/CITAC Guide, 1st Ed. (2003) “Traceability in chemical measurement”
[5] ISO/IEC 17025, 2nd Ed. (2005), “General requirements for the competence of testing and calibration laboratories”
[6] ISO Guide 34:2009, “General requirements for the competence of reference material producers”
[7] DIN EN ISO 15212-1:1998, Oscillation-type density meters - Part 1: Laboratory instruments
[8] Reichmuth, A., Wunderli, S., Weber, M., Meyer, V. R. (2004), “The uncertainty of weighing data obtained with electronic analytical balances”, Microchimica Acta 148: 133-141.
[9] Calculated by combination of the squared contribution values

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fumasep® FAB-PK-130

General

Membrane type: Anion-exchange membrane - PK-reinforced - thickness 130 µm - with high proton blocking capability, high selectivity, very high mechanical stability, and high stability in acidic and caustic environment.

Application: Electrodialysis and electrodialysis with bipolar membranes.

Membranes are identified by membrane type and identification number (Lot No). Please refer to this type and identification number in case of queries.

Delivery

The membrane is the brown foil delivered in dry form.

Handling and Storage

Keep membrane package closed / sealed when unused. Unpack membrane only for direct use and process immediately after opening. Store, handle and process the membrane in a clean and dust-free area.

Always wear protective gloves when handling the membrane. Handle with care, be sure not to puncture, crease or scratch the membrane, otherwise leaks will occur. All surfaces which may get into contact with the membrane during inspection, storage, pretreatment and mounting must be free of sharp edges or angles.

Dry form: Storage for long time scale (> 12 month) may be done in dry state (sealed container). Wet form: Storage for short and medium time scale (hours up to several weeks) may be done in unsealed containers in 0.5 – 1.5 wt% NaCl solution or comparable neutral pH electrolytes. For storage over a longer time period a sealed container is recommended using afore said electrolyte with ca. 100 ppm biocide (NaN_3) to avoid biological fouling.

Pretreatment

The membrane is delivered in bromide form and dry form. Depending on application and cell design, assembling is possible in dry (without pretreatment) or wet form. Pretreatment before assembling: Put the membrane sample between stabilizing meshes / spacers (in order to avoid curling) in NaCl solution - e.g. 0.5 M NaCl solution at T = 25 °C for 72 hrs exchanging several times the solution. Do not let the membrane dry out since micro-cracks may likely occur during shrinkage.

If you have any concerns about storage, chemical stability, pre-treatment or before proceeding, please feel free to contact us for further information.

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Fax: +49-(0)-7142-3737-999
Email: sales@fumatech.com

fumatech
Funktionelle Membranen und Anlagentechnologie
BWT GROUP

Technical Data Sheet - fumasep® FAB-PK-130

Physical and chemical data

fumasep®		**FAB-PK-130**
membrane type		anion exchange membrane
appearance / colour		brown, transparent
backing foil		none
reinforcement		PK
counter ion		bromide (Br^-)
delivery form		dry
thickness (dry)	µm	115 – 138
ion exchange capacity (as chloride form, based on membrane incl. reinforcement layer)	meq g^{-1}	0.8
specific conductivity in Cl^- form [a)]	mS cm^{-1}	> 2,5
area resistance in Cl^- form [a)]	Ω cm^2	< 4
selectivity 0.1 / 0.5 mol/kg KCl at T = 25 °C [b)]	%	> 95
uptake in H_2O at T = 25 °C [c)]	wt %	14
dimensional swelling in H_2O at T = 25 °C [d)]	%	0
proton transfer rate [e)]	µmol min^{-1} cm^{-2}	< 500
bubble point test in water at T = 25 °C	bar	> 3
Young's modulus at 23 °C / 50 % r.h. [f)]	MPa	> 1200
yield strength at 23 °C / 50 % r.h. [f)]	MPa	n.a.
tensile strength at 23 °C / 50 % r.h. [f)]	MPa	50 – 70
elongation at break at 23 °C / 50 % r.h. [f)]	%	21 – 35

a) in Cl^- form in 0.5 M NaCl @ T = 25 °C, measured in standard measuring cell (through-plane).
b) determined from membrane potential measurement in a concentration cell.
c) in Br^- form, membrane as received stored in water for 24 hrs, reference membrane dried over P_2O_5 *in vacuo*.
d) in Br^- form, membrane as received stored in water for 24 hrs, reference membrane as received.
e) determined from pH potential measurement in a concentration cell 0.1 M HCl / 0.1 M KCl @ T = 25 °C.
f) in Br^- dry form, membrane as received, determined by stress-strain measurement at T = 25°C and 50 % r.h., DIN EN 527-1.

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Email: sales@fumatech.com

fumasep® FKB-PK-130

General

Membrane type: Cation-exchange membrane - PK-reinforced - thickness 130 µm, with low resistance, high selectivity, very high mechanical stability, high stability in pH-acidic and caustic environment, and high OH blocking capability.

Application: Electrodialysis and electrodialysis with bipolar membranes.

Stability range: Stable under caustic conditions (e.g. 4 M KOH) at T = 25 °C.

Membranes are identified by membrane type and identification number (Lot Number). Please refer to this type and identification number in case of queries.

Delivery

The membrane is the brown foil delivered in dry form.

Handling and Storage

Keep membrane package closed / sealed when unused. Unpack membrane only for direct use and process immediately after opening. Store, handle and process the membrane in a clean and dust-free area. Use only new and sharp knives or blades, when cutting the membrane. Always wear protective gloves when handling the membrane. Handle with care, be sure not to puncture, crease or scratch the membrane, otherwise leaks will occur. All surfaces in contact with the membrane during handling, inspection, storage and mounting must be smooth and free of sharp projections.

Dry form: Storage for short and medium time scale (up to several months) may be done in dry state (sealed container). Wet form: Storage for short and medium time scale (hours up to several weeks) may be done in unsealed containers in 0.5 - 1.5 wt% NaCl solution or comparable neutral pH electrolytes. For storage over a longer time period a sealed container is recommended using afore said electrolyte with ca. 100 ppm biocide (e.g. NaN_3) to avoid biological fouling.

Pretreatment

The membrane is delivered in H-form and dry form. Depending on application and cell design, assembling is possible in dry (without pretreatment) or wet form. Before assembling in wet form put the membrane sample between stabilizing meshes / spacers (in order to avoid curling) in NaCl solution - e.g. 0.5 M NaCl solution at T = 25 °C for 72 hrs exchanging the solution several times. Do not let the membrane dry out since micro-cracks may likely occur during shrinkage.

If you have any concerns about storage, chemical stability, pre-treatment or before proceeding, please feel free to contact us for further information.

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Email: sales@fumatech.com

Physical and chemical data of fumasep® FKB-PK-130

fumasep®		**FKB-PK-130**
membrane type		cation exchange membrane
appearance / colour		brown, slightly opaque
reinforcement		PK
counter ion		protonic form (H^+)
delivery form		dry
supporting foil		none
thickness (dry)	µm	126 – 140
weight per unit area	mg cm^{-2}	15 – 22
ion exchange capacity (as sodium form)	meq g^{-1}	0.9
specific conductivity in Na^+ form [a)]	mS cm^{-1}	> 2,5
area resistance in Na^+ form [a)]	Ω cm^2	< 4,5
selectivity 0.1 / 0.5 mol/kg KCl at T = 25 °C [b)]	%	> 96
uptake in H_2O at T = 25 °C [c)]	wt %	14
dimensional swelling in H_2O at T = 25 °C [d)]	%	0
bubble point test in water at T = 25 °C	bar	> 3
Young's modulus at 23 °C / 50 % r.h. [e)]	MPa	> 1200
yield strength at 23 °C / 50 % r.h. [e)]	MPa	–
tensile strength at 23 °C / 50 % r.h. [e)]	MPa	45 – 70
elongation at break at 23 °C / 50 % r.h. [e)]	%	24 – 48

a) in Na^+ form in 0.5 M NaCl @ T = 25 °C, measured in standard measuring cell (through-plane).
b) determined from membrane potential measurement in a concentration cell.
c) in H^+ form, membrane as received stored in water for 24 hrs, reference membrane dried over P_2O_5 *in vacuo*.
d) in H^+ form, membrane as received stored in water for 24 hrs, reference membrane as received.
e) in H^+ form, membrane as received, determined by stress-strain measurement at T = 25°C and 50 % r.h., DIN EN 527-1.

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fumasep® FBM

General

The fumasep® FBM single film Bipolar Membrane consists of an anion exchange layer and a cation exchange layer manufactured using a patented multilayer-coating production technology.

This composite membrane is chemically stable and mechanically reinforced with woven PEEK. In the intermediate layer between anion exchange layer (AEM) and cation exchange layer (CEM) water is catalytically active to force dissociation of water into OH^- and H^+– ions when exceeding a potential difference of approximately 0.8 V. The membrane should be operated under forward bias conditions which may cause blistering. The CEM must be directed towards the cathode, the AEM must be directed towards the anode. If the membrane is used in the wrong position at high current density even for short term, the interim layer may degrade (blistering), and the monolayers may delaminate.

The electro-catalytically forced water dissociation produces – in contrast to the classical electrolysis of water – no reaction gases. Therefore, one Mol of OH^- and H^+ – ions can be achieved at an energy value of approximately 22 Wh (Electrolysis: approximately 55 Wh per Mol).

The fumasep® FBM membranes are easy to use and show:

- High water splitting efficiency (>98% at 100 mA cm^{-2} in 0.5 M NaCl @ 25 °C)
- Low water splitting voltage (< 1.2 V at 100 mA cm^{-2} in 0.5 M NaCl @ 25 °C)
- Excellent mechanical properties at low thickness (0.13 – 0.16 mm)

Membranes are identified by membrane type and identification number (Lot.-Number). Please refer to this type and identification number in case of queries.

Delivery

The membrane is the brown foil delivered in wet form.

Handling and Storage

Please pay attention that the membrane surface is not contaminated with surface active agents or will be damaged by mechanical influence.

High attention must be given to the right polarity when using the membranes!

When mounting the membranes it is imperative that the membrane sides will not get mixed up. Therefore, the cation side is marked with '***cathode side***'. This side must be directed towards the cathode (see also drawing overleaf).
The membrane should be stored in 1 M NaCl-solution and placed in a closed container. If storage will be for a longer period of time 100 ppm of NaN_3 should be added to prevent biological growth. Other biocides have not been used as yet.

The membrane is not stable against chlorine (Cl_2).

If you have any concerns before proceeding, please feel free to contact us for further information

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fumasep®		FBM
membrane type		bipolar
appearance / colour [a]		brown
backing foil		none
reinforcement		PK
counter ion		Na (CEM layer) / Cl (AEM layer)
delivery form		wet in NaCl solution
thickness (dry)	µm	130 - 160
weight per unit area (dry)	mg cm^{-2}	15 - 17
dimensional swelling H_2O at T = 25 °C [b]	%	0
water splitting voltage at 100 mA cm^{-2} [c]	V	< 1.2
water splitting efficiency at 100 mA cm^{-2} [c]	%	> 98
maximum operation temperature	°C	40

a) the color and the surface of the product may vary slightly.
b) reference membrane as received
b) in 0.5 M NaCl solution and 0.25 M Na_2SO_4 electrode rinse solution at 25 °C.

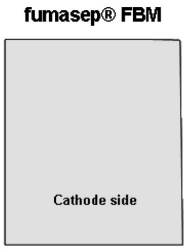
Note: The product is not certified for drinking water applications. The data are not measured directly on the item supplied. The data sheet does not release the customer of the necessity of a goods inwards control procedure. All information included in this data sheet is based on tests and data believed to be reliable. The data do not imply any warranty or performance guarantee. It is the user's responsibility to examine performance, suitability and durability of the product for the intended purpose. FUMATECH BWT GmbH does not assume any liability for patent infringement resulting from the use of this product.
Hereby, it is certified that all results of the measured item comply with the margins of the internal specification defined in the technical datasheet. All measurements and data recording are conducted in accordance with standardized procedures following the ISO 9001 certification.

Pretreatment

The membrane is delivered in wet form and ready to use. Additional cleaning is required by rinsing the membrane either in the application solution or a NaCl solution according to the application requirement. Assembling is possible in wet form only. Do not let the membrane dry out since micro-cracks may likely occur during shrinkage.

If you have any concerns about storage, chemical stability, and pretreatment please feel free to contact us for further information.

See following drawing for correct orientation of the membrane side. The cation exchange side is marked with '***cathode side***'.



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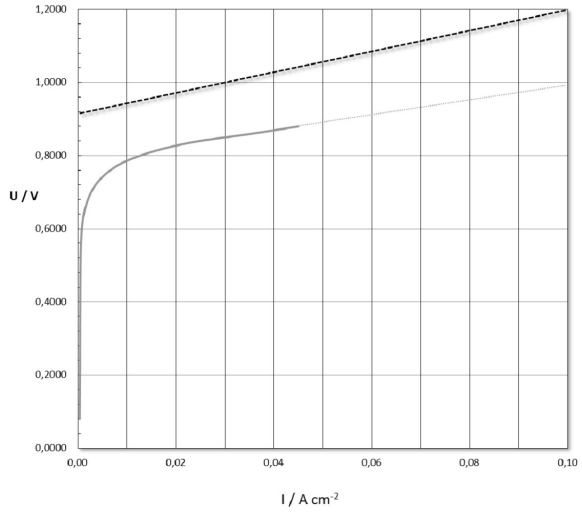
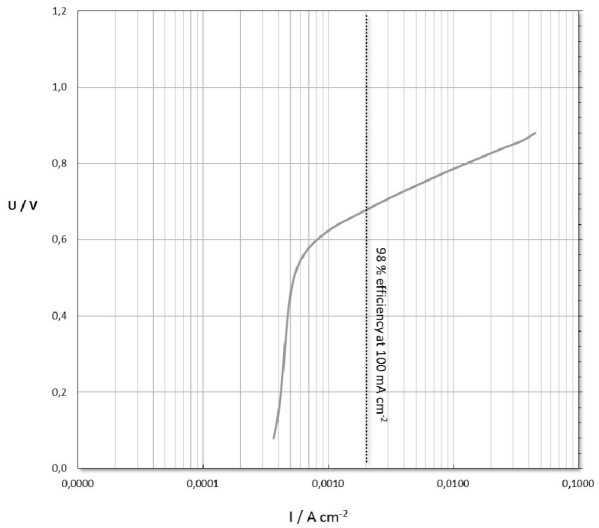
Technical Data Sheet fumasep® FBM

Current – Voltage Characteristics: fumasep® FBM

4-chamber set-up: cathode – Na_2SO_4 – CEM – NaCl – FBM – NaCl – CEM – Na_2SO_4 solution – anode
4-probe measurement: Haber-Luggin capillary (3 M KCl) with Ag / AgCl reference electrodes
CEM: Cation exchange membrane FKB
electrolyte loop: 0.5 M NaCl solution / recombined
electrode loop: 0.25 M Na_2SO_4 / recombined
temperature: 25 °C
fixed scan rate, ΔU = 20 mV, Δt = 20 s





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