

Determination of ions in ash using ion-selective electrodes



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-Divisha Saxena

Abstract

The aim of this research work is to evaluate suitability of ion-selective electrodes for determination of Na^+ , K^+ , Cl^- , CO_3^{2-} and pH in electrostatic precipitator (ESP) ash samples from a recovery boiler provided by Andritz Oy. The ash composition is an important detail for soot blowing (cleaning) of a recovery boiler and an approximate concentration range of Na^+ , K^+ , Cl^- , CO_3^{2-} and SO_4^{2-} in the ash samples has been provided from Andritz analysis database. K and Cl composition is the most important parameter for the fouling analysis. This research work involves preparation and testing of multi-ion standard (calibration) solutions and PVC membrane-based carbonate-selective electrodes. Commercial ion-selective electrodes are used for Na^+ , K^+ , Cl^- and pH measurement and a carbonate-selective electrode prepared in our lab was used for estimation of CO_3^{2-} content in the ash samples. The SO_4^{2-} content (mass %) is calculated as remaining ions in the solution. Due to the relatively high ion concentrations in the samples, a very low limit of detection is not needed here, while the electrode selectivity and stability (ruggedness) are important. The Na^+ , K^+ , Cl^- , CO_3^{2-} and SO_4^{2-} are always present in an estimated range in the ash samples. This work focuses on the accuracy and precision of ion measurements with ion-selective electrodes.

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1. Introduction

The main objective of this thesis is to comprehend the suitability of ion-selective electrodes in the analysis of fly ash samples collected from the outlet of electrostatic precipitators in a Kraft recovery boiler. A recovery boiler is an important component of a pulp mill, and one of its main purposes is the combustion of concentrated black liquor which contains organic dissolved wood residues to produce heat [1]. This heat is used in power and steam generation. A recovery boiler is also responsible for recovering cooked chemicals that can be re-cycled, reducing chemical consumption as well as reusing cooked chemicals that would otherwise be wasted.

The flue gases generated from the recovery boiler after the combustion of black liquor are a mixture of volatile matter, carbon, and “fly ash”. The properties and behaviour of fly ash depend upon black liquor composition and combustion conditions. Fly ash does not have a certain melting point, but a range of melting temperatures, i.e., first melting temperature (T_0), sticky temperature (T_{15}), flow temperature (T_{70}) and liquid temperature (T_{100}). These temperatures are determined using the chemical composition of ash and can be helpful in predicting fouling conditions in the boiler. Fouling mechanisms have always been a matter of concern in recovery boiler design and operations; therefore, several studies have been reported to date on recovery boiler plugging and fouling mechanisms [2].

The purpose of this work is to analyse these ash samples and quantify the Na^+ , K^+ , Cl^- , and CO_3^{2-} ions present in the ash using ion-selective electrodes (ISEs). The SO_4^{2-} concentration is estimated as rest of the ash content. There have been various studies on the effect of potassium and chloride compositions on fouling mechanisms in the recovery boilers. Potassium (K) and chlorine (Cl) lower the melting temperature of the ash formed in the recovery boiler, which increases fouling and sticking tendencies and therefore can largely affect the recovery boiler's operation [3,4]. The higher the amount of K and Cl present in the black liquor and hence in the fly ash formed, the higher the risk of corrosion and fouling of the boiler, and therefore it is important to keep these parameters in check to ensure proper clean-up regularly and to avoid unprecedented boiler shut-down due to excessive fouling.

The ISEs enable us to quantitatively estimate the presence of one chemical species selectively in the presence of other species in the same solution [5]. The signal response is proportional to the concentration or activity of the species. One of the most widely used chemical sensors in chemical, environmental, industrial, and laboratory analyses are ion-selective electrodes, which belong to electrochemical (potentiometric) chemical sensors [6].

The operating principle of ISEs is based on potentiometry. Potentiometry is an important electroanalytical technique that measures the potential developed in a system using a combination of electrodes. The mid-1960s marked the beginning of modern potentiometry, which can be considered a classical method for ion analysis. In terms of practical impact and commercial success, potentiometry has become the standard technique in the clinical analysis of ions like Na^+ , K^+ and Cl^- today [7].

ISEs provide a portable and selective solution for ion analysis and can produce reproducible, reversible, and fast responses. They are also characterized by their small size, low costs, and low energy consumption, which makes them an attractive choice for practical applications such as environmental, clinical as well as industrial analyses. Considering their simple operation and ability to provide accurate and reliable direct and continuous measurements, ISEs are a distinct choice in pharmaceutical analyses too [8]. Due to these factors, ion-selective electrodes are widely available commercially and are one of the most practical chemical sensors.

In this work, commercial sodium, potassium, and chloride-selective electrodes were used for estimation of the respective ion contents in standard solutions, to prepare the calibration plots, and for the analysis of different ash samples. For pH measurements, a Mettler Toledo pH meter was used, and silver-silver chloride reference electrode ($\text{Ag}|\text{AgCl}|\text{3M KCl}|\text{1M LiOAc}$) was used as a reference electrode during potentiometric measurements. For estimation of CO_3^{2-} content, a carbonate-selective electrode was prepared and used. The SO_4^{2-} content, as aforementioned, was calculated as the rest of the content of the ash (in mass%).

2. Theory

2.1. Chemical sensors

Chemical sensing is an information acquisition process that enables us to obtain the chemical composition of the system in real-time [9]. A chemical sensor, in general, consists of two mechanisms combined: molecular recognition and signal transduction. The basic principle of chemical sensors is that a signal can be produced and amplified by a physical transducer combined with a selective material that is responsible for molecular recognition. The signal produced is interpreted to provide information about the chemical species present in the medium. There are four main principles of signal transduction: electrochemical, optical, mass, and thermal sensing.

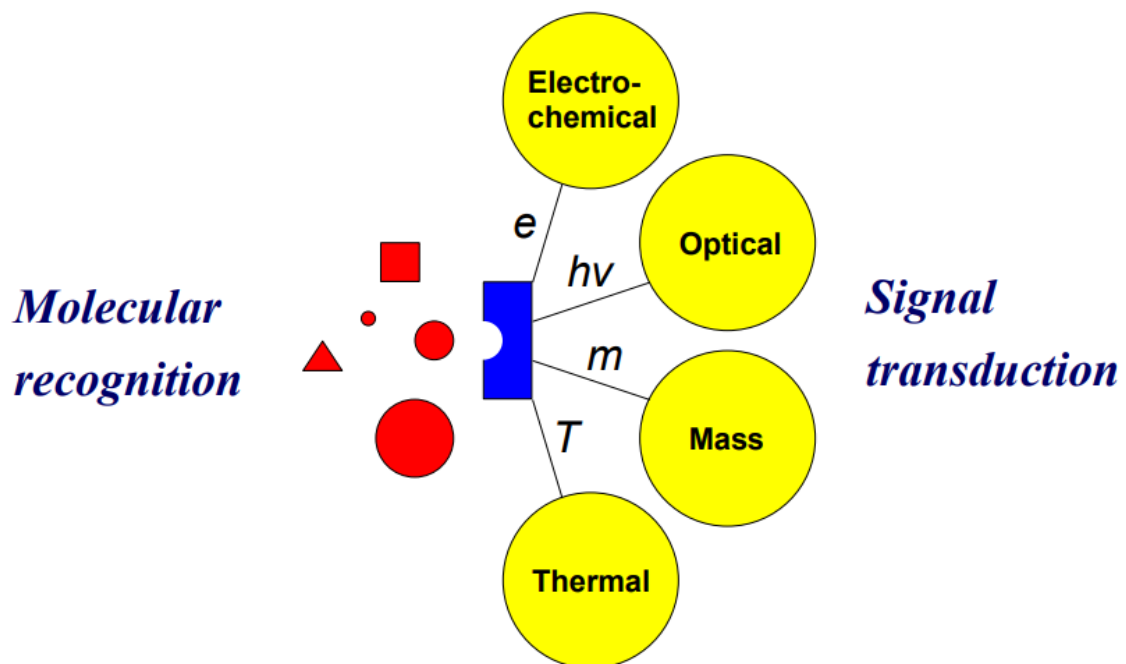


Fig 1. Signal transduction principles (Johan Bobacka, Lecture in Chemical Sensors and Biosensors, Åbo Akademi University, 2022.)

2.1.1. General response curve and sensitivity

A chemical sensor produces “response” due to a chemical stimulation. The physical change that causes the stimulation depends on the sensor and the sensing environment [9]. A general response curve relates the response given by the sensor to the analyte concentration. Besides the analyte, the interferences also interact with the selective material. According to EURACHEM Guide, the “analytical sensitivity” is the change in instrument response with respect to change in measured quantity (e.g., analyte concentration), which is given by the gradient of the response curve [10,11].

2.1.2. Characteristics

The most important characteristic of a chemical sensor is its selectivity, as it determines its usefulness in a particular application. Selectivity as the name suggests, is the capability of a sensor to respond selectively to a chemical species in presence of possible interferences. Another important characteristic of a sensor is ruggedness. Especially in process analytical applications, ruggedness is one of the most important factors for choosing a sensor. Ruggedness means ability of a device to give a stable and reliable signal under varying conditions. Additionally, reversibility, portability and long-term stability and costs are some important factors to be considered while choosing a chemical sensor.

2.2. Electrochemical sensors

Electrochemical methods for chemical detection are widely used in industrial process control, effluent monitoring, and environmental and pharmaceutical analyses. The simple nature of electrochemical parameters (e.g., potential change or charge transfer) facilitates signal detection using modern electronics, and therefore helps in data collection and interpretation effectively [9]. Potentiometry and amperometry are the two basic principles on which most of the electrochemical sensors are based.

Potentiometry is a classical analytical technique, but the rapid development of modern electronics and more sensitive and selective electrodes since the 1970's expanded greatly the analytical applications of potentiometry [12]. Potentiometric measurements can be useful where rapid, inexpensive, and accurate chemical analysis is desired. Both pH electrodes and ion-selective electrodes (ISEs) are based on the principle of potentiometric chemical sensors. ISEs are one of the oldest chemical sensors and they bridge the fundamentals of membrane science with host-guest chemistry [12]. The potentiometric sensors and the principle of potentiometry is described in the following sections.

2.3. Potentiometric chemical sensors

Potentiometric measurements are done in zero-current conditions [9]. It typically uses a two-electrode system consisting of an indicator electrode (ion-selective electrode) and a reference electrode. The potential difference between indicator and reference electrode is measured using a potential-measuring device (a pH meter or a millivolt meter). The reference electrode ideally has constant or steady potential and as the name suggests provides the reference potential value. Ideally, the potential response of the ISE with respect to change in ion activity at zero current conditions is governed by the following equation:

$$E = E^{\circ} + (2.303 RT/z_i F) \log a_i \quad (1)$$

where, E is the electrode potential response; E° is constant potential value that includes sample independent potential contributions; R is the universal gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$); T is the absolute temperature (in Kelvin); F is the Faraday constant; z_i and a_i are the ionic charge and activity of the target ion respectively.

Equation 1 suggests that the electrode potential response is directly proportional to the logarithmic value of activity of the analyte ions. For monovalent ions ($z_i=1$) a tenfold change in activity results in change of electrode potential by 59.1 mV ideally (at 298 K). Similarly, for divalent ions ($z_i=2$), a similar change in activity should change the electrode response by 29.6 mV. This response is called "Nernstian behaviour" where a change of electrode response by 1 mV characterizes ca 4% and ca 8% change in activity respectively for monovalent and divalent ions [12].

We should consider that the ISEs respond to the ionic activity rather than the concentration. The term activity (a_i) denotes the effective ion concentration due to interaction of ions with oppositely charged species. The activity of an ion i can be related to its concentration (C_i) in the solution by the following equation:

$$a_i = \gamma_i C_i \quad (2)$$

where, γ_i is the activity coefficient. The activity coefficient is dependent on the ionic species present as well as the total ionic strength of the solution. The total ionic strength depends on the concentration and ionic charge of all ionic species present in the solution.

For the chemical analysis, we are often more interested in the total concentration rather than activity of the ion. To overcome this, the standard solutions used for plotting the calibration graph should have similar ionic strength and composition as the samples.

Combining equation (1) and (2), we get the following expression:

$$E = [E^o + (2.303 RT/z_i F) \log \gamma_i] + (2.303 RT/z_i F) \log C_i \quad (3)$$

In equation 3, the terms in squared bracket represent constant potential for solutions with similar ionic activity and it is developed due to ionic interactions and other constants of measurement such as, liquid junction potential and instrumentation potential [9].

2.3.1. Components of potentiometric cells

The two main components of a potentiometric cell are indicator electrode and the reference electrode, including the liquid junction as shown in the fig. 2. The indicator or the ion-selective part gives a potential response which is measured against a reference potential value provided by the reference electrode. The reference electrode itself is related to a standard potential value given by Standard Hydrogen electrode. The operating principles of the two components (e.g., reference electrode and ion-selective electrode) are discussed in brief in the following sections.

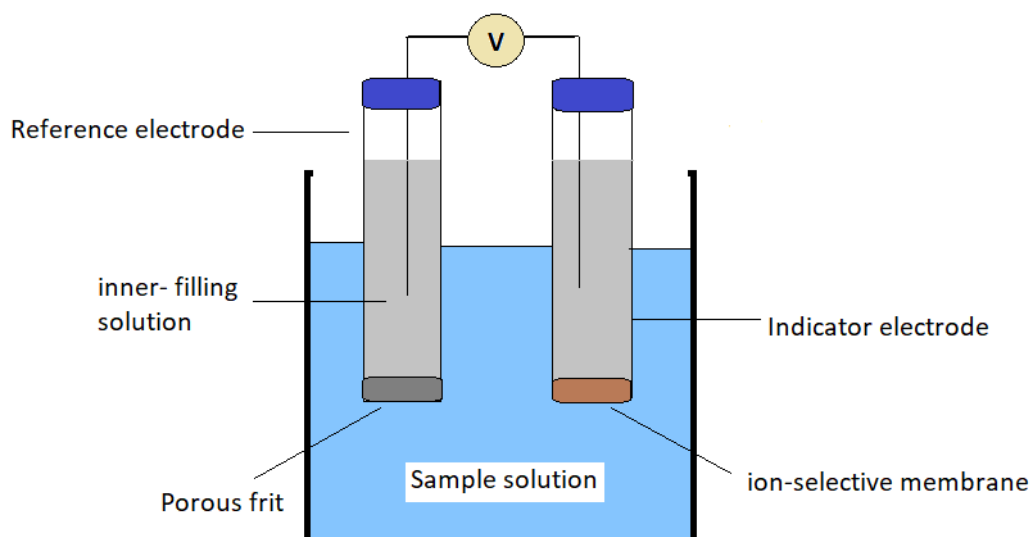


Fig 2. General scheme of a potentiometric cell

2.4. Reference electrodes

The reference electrode is responsible for giving a reference potential value against which the potentiometric measurement can be done using an indicator electrode. For example, a silver/silver chloride reference electrode, with saturated KCl is a secondary kind of reference electrode, and its potential is +0.197 V at 25°C, against the standard hydrogen electrode [9]. The standard hydrogen electrode (SHE) is a primary reference electrode which is established to have potential 0 V under standard conditions.

The three most desirable characteristics of a good reference electrode are potential stability, reversibility, and reproducibility. Stability, in this context means the reference electrode should be able to give a stable and constant potential on changing the measured solutions. It should be reversible in nature, so that it returns to its equilibrium potential very fast after small transient perturbation [9]. The reproducibility condition is satisfied if the electrode can give the same potential response when constructed with the same electrode materials and filling solution combination and operated under similar physical conditions.

Another important characteristic of reference electrodes is that they should ideally be unpolarizable, which means that the electrode potential remains practically constant even if a small current is flowing through the electrode. Therefore, any potential change observed in the system can be attributed to the indicator electrode [9].

2.5. Ion-selective electrodes (ISEs)

Ion-selective electrodes (ISEs) are the type of chemical sensors based on electrochemical (potentiometric) signal transduction principle. This means that the analyte recognition takes place by measuring the potential change observed in the system due to activity of target ions present in the sample to be analysed. The ion-selective membrane (ISM) is the primary component of the ISE, which enables ion recognition and is selective to a particular ion depending on the ionophore used.

2.5.1. Ion-selective interface

The ISM/solution interface is also called as perm-selective interface and is found in ion-selective sensors e.g., ion-selective electrodes and ion-selective field effect transistors [9]. The ion-selective membrane separates the sample from the inside of the electrode and is the key component of all potentiometric sensors, as it establishes its selectivity towards the ion of interest in the presence of other ions in the same solution. The ion-selective membrane is usually non-porous, mechanically stable, insoluble in water, and designed in a way that the potential response is primarily due to target ions (via selective binding process, e.g., ion complexation) [12].

The ISEs can be classified into different types based on the type of ion-selective membrane used:

- Glass membranes: e.g., pH electrodes, Sodium ISE.
- Crystalline membranes: solid state membranes based on inorganic salts, e.g., Fluoride ISEs have a monocrystalline lanthanum fluoride LaF_3 membrane.

- Polymeric membranes: ionophore is embedded on a polymer matrix, usually plasticized PVC, e.g., Potassium ISE is a polymer PVC matrix membrane electrode.
- Compound electrodes: e.g., gas electrodes, enzyme electrodes.

For practical applications, the working range (linear concentration range), response slope, selectivity, response time, reproducibility, and the stability of these characteristics of an ISE over a period of time are the characteristics of utmost importance. The experimental procedure determining these characteristics remains independent of the type of ISE, whether it is a glass, polymeric or solid-state membrane electrode.

2.5.2. Working range and response slope

In conventional ion-selective electrodes, the ion-selective membrane is in contact with the sample solution and the electrode contains an inner filling solution with constant ion activity. The response is the potential difference established between the membrane and the sample solution. The working range and response slope are determined by the calibration curve. A calibration curve can be obtained by plotting the potential response (mV) versus logarithmic values of known concentration (activity) of the ion of interest in the standard solutions.

2.6. Applications

Generally, ISEs do not require sample pre-treatment or complex sample preparation before analysis, which makes them widely suitable for continuous monitoring in clinical, industrial, and environmental applications. ISEs along with the instrumentation required for measuring the potentiometric signals are rather inexpensive in comparison to other analysis techniques, have lower power consumption and are easier to operate [6]. These advantages have led to ISEs being used diversely in various industrial segments like agriculture, biomedical applications, electroplating, environmental analysis, food industry, pulp and paper production, power generation and pharmaceutical industries to name a few. Today, ISEs are widely used for research and education purposes, on-line analysis, production monitoring and quality control [13].

2.6.1. Potassium-selective electrodes

The commercial potassium ISE (Mettler Toledo DX239-K) used in this work is widely used today in applications requiring estimation of potassium ion concentration. These applications include wastewater analysis, estimation of potassium content in wine, fruit juice, milk etc., and in fertilizer analysis. Potassium ISE, a polymer-based membrane electrode, typically uses valinomycin as an ionophore, which provides selectivity towards potassium ions present in the sample solution. The measured potential response is based on chemical equilibrium between the K^+ ions present in the standard or sample solutions and the ion-selective membrane [14].

2.6.2. Sodium-selective electrodes

Sodium-selective electrodes (Mettler Toledo DX222-Na) used here are a typical example of glass membrane electrodes used commercially. Similar to pH electrodes, Na ISEs also belong to glass membrane electrodes category, but they use membrane glass with higher selectivity towards sodium ions. There are glass membranes for Na^+ , K^+ , Li^+ and, Ag^+ assay, but among these only Na^+ glass electrodes are used in practical applications [6]. Some of the most common applications include food (milk, fruit juice, beef broth, tea, wine) and water (drinking water, boiler water, sea water) analysis and clinical applications, e.g., blood serum analysis [13]. Generally, glass membrane electrodes have better chemical resistance and give faster response in comparison to polymeric membrane electrodes.

2.6.3. Chloride-selective electrodes

Chloride ISE (Mettler Toledo DX235-Cl) used in this work is a solid-state membrane electrode, available commercially for several practical applications, e.g., in clinical and agricultural analysis [15]. The Chloride-selective electrodes are also commonly used in food and water analysis. A polycrystalline or mixed crystal membranes such as $AgCl/Ag_2S$ is the ion-selective interface which determines Cl^- ions present in standard or sample solutions. Crystalline (solid-state) membrane electrodes are known to be more robust, can provide a longer lifetime, and show significantly lower resistance in comparison to glass and polymer membranes [6,13].

2.6.4. Carbonate-selective electrodes

In 1974, a liquid membrane electrode was developed by Herman and Rechnitz which showed high selectivity towards carbonate ion that is suggested to be suitable for biological, chemical, and oceanographic measurements [16]. Since then, there has been great amount of research in development of carbonate-selective electrodes, using derivatives of trifluoroacetophenone as carbonate ionophore [17]. The carbonate-selective electrodes used in this work were prepared in the Åbo Akademi laboratory based on a previous thesis work on “Determination of Carbonic Acid Species Using Carbonate- and Novel Bicarbonate-Selective Electrodes” by J. G. Gamaethiralalage [18]. These electrodes were prepared by immobilizing carbonate ionophore (N,N-Dioctyl-3 α ,12 α -bis(4-trifluoroacetylbenzoyloxy)-5 β -cholan-24-amide) in a plasticized PVC matrix. The principle of construction of carbonate-selective electrodes is explained further in section 3.6. It is also important to mention that the form in which carbonic species are present is largely dependent on the pH of the solution [19].

3. Experimental Design and Procedure

Potentiometric measurements were done using a multi-channel mV-meter to allow simultaneous measurements of several ions and pH. Three multi-ion standard solutions used as calibration solutions containing all the measured ions (Na^+ , K^+ , Cl^- , CO_3^{2-}) were prepared from KCl, NaCl, K_2SO_4 , Na_2SO_4 and Na_2CO_3 to calibrate all the ISEs simultaneously before measurements.

3.1. Instruments

- Lawson Labs EMF 16 Channel Multi-voltmeter (Malvern, PA, USA)
- Mettler Toledo AG204 analytical balance
- Metrohm Double Junction Ag|AgCl|3M KCl|1M LiOAc reference electrode
- Mettler Toledo DX239-K potassium electrode
- Mettler Toledo DX222-Na sodium electrode
- Mettler Toledo DX235-Cl chloride electrode
- Mettler Toledo InLab Expert pH electrode
- Mettler Toledo S20 SevenEasy pH meter
- Mettler Toledo FiveEasy conductivity meter

3.2. Software

- EMF Suite version 2.0

3.3. Chemicals used

| Reagent | Molar Mass (gmol/L) | Purity | Make |
|---|---------------------|---------|----------------|
| TDMACl ^I | 572.47 | Unknown | Sigma Aldrich |
| DOA ^{II} | 370.57 | ≥ 99% | Sigma Aldrich |
| PVC ^{III} | High molecular wt. | Unknown | Sigma Aldrich |
| Carbonate Ionophore ^{IV} | 1016.24 | Unknown | Sigma Aldrich |
| THF ^V | 72.11 | 99.5% | Sigma Aldrich |
| EtOAc ^{VI} | 88.11 | >99.5% | Fluka |
| NaCl | 58.44 | ≥ 99.5% | Merck |
| Na ₂ CO ₃ | 105.99 | ≥ 99.0% | Sigma Aldrich |
| K ₂ SO ₄ | 174.27 | 99.0% | Merck |
| NaH ₂ PO ₄ .2H ₂ O | 177.99 | 99.5% | Merck |
| Na ₂ HPO ₄ | 141.96 | 99.9% | J.T. Baker |
| KCl | 74.55 | 99.5% | Sigma Aldrich |
| Na ₂ SO ₄ | 142.04 | 99% | Riedel-de Haen |

I - Tridodecylmethylammonium chloride,

II - Bis(2-ethylhexyl) adipate, "

III - Polyvinyl chloride,

IV - N,N-Dioctyl-3 α ,12 α -bis(4-trifluoroacetylbenzoyloxy)-5 β -cholan-24-amide (Carbonate Ionophore VII),

V - Tetrahydrofuran,

VI - Ethyl Acetate

3.4. Expected concentrations in ash samples

The expected concentrations (in mass %) of Na⁺, K⁺, Cl⁻, CO₃²⁻ and SO₄²⁻ in the ash samples (Table 1) have been taken from Andritz analysis database which was used to estimate the concentration of the standard solutions.

Table 1. Expected concentrations of ions in ash samples

| Sample, mass % | K ⁺ | Cl ⁻ | Na ⁺ | CO ₃ ⁻² | SO ₄ ⁻² |
|----------------|----------------|-----------------|-----------------|-------------------------------|-------------------------------|
| average | 4.49 | 2.70 | 30.81 | 11.71 | 49.89 |
| min | 0.18 | 0.10 | 20.70 | 0.20 | 26.20 |
| max | 18.20 | 11.40 | 37.20 | 33.20 | 65.90 |

3.5. Preparation of calibration solutions

Three calibration solutions were prepared to span the expected concentration ranges for all measured ions. The approximated total ionic strength of each solution is 0.110 mol/L. The pH and electrical conductivity of each solution were also measured, and their ionic strength is respectively calculated in the next section.

Table 2 shows the different salts (and concentrations) used to prepare the calibration solutions, which were used as standards in the analysis and for calculating the linear response of the ion-selective electrodes. The ion concentrations of the standard solutions are shown in Table 3.

Table 2. Calibration solutions salt concentrations

| Salt | Calibration Solution 1 (mmol/L) | Calibration Solution 2 (mmol/L) | Calibration Solution 3 (mmol/L) |
|---------------------------------|------------------------------------|------------------------------------|------------------------------------|
| KCl | 1.00 | 0.00 | 0.00 |
| NaCl | 20.00 | 3.00 | 0.30 |
| K ₂ SO ₄ | 0.00 | 3.50 | 26.55 |
| Na ₂ SO ₄ | 10.00 | 27.50 | 9.35 |
| Na ₂ CO ₃ | 20.00 | 5.00 | 1.00 |

Table 3. Calibration solutions ionic concentrations

| Ion | Calibration Solution 1 | | Calibration Solution 2 | | Calibration Solution 3 | |
|-------------------------------|----------------------------|--------|----------------------------|--------|----------------------------|--------|
| | Concentration (C) mol/L | log C | Concentration (C) mol/L | log C | Concentration (C) mol/L | log C |
| Na ⁺ | 0.080 | -1.097 | 0.068 | -1.167 | 0.021 | -1.678 |
| K ⁺ | 0.001 | -3.000 | 0.007 | -2.155 | 0.053 | -1.275 |
| Cl ⁻ | 0.021 | -1.678 | 0.003 | -2.523 | 0.000 | -3.523 |
| SO ₄ ⁻² | 0.010 | -2.000 | 0.031 | -1.509 | 0.036 | -1.445 |
| CO ₃ ⁻² | 0.020 | -1.699 | 0.005 | -2.301 | 0.001 | -3.000 |

These calibration solutions will be used to plot a calibration graph (potential vs. log C) by measuring the response of the respective ion-selective electrodes using Lawson Labs EMF 16 channel multi-voltmeter.

The following amount of chemicals were weighed using an analytical balance to prepare the standard solutions (Table 4):

Table 4. Calibration solutions – calculated and weighed salt amount

| Salt (grams) | Calibration Solution 1 | | Calibration Solution 2 | | Calibration Solution 3 | |
|---------------------------------|------------------------|---------|------------------------|---------|------------------------|---------|
| | calculated | weighed | calculated | weighed | calculated | weighed |
| KCl | 0.0746 | 0.0747 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| NaCl | 1.1688 | 1.1687 | 0.1753 | 0.1752 | 0.0175 | 0.0176 |
| K ₂ SO ₄ | 0.0000 | 0.0000 | 0.6099 | 0.6100 | 4.6269 | 4.6270 |
| Na ₂ SO ₄ | 1.4204 | 1.4204 | 3.9061 | 3.9062 | 1.3281 | 1.3283 |
| Na ₂ CO ₃ | 2.1198 | 2.1197 | 0.5299 | 0.5300 | 0.1060 | 0.1060 |

3.6. Preparation of carbonate-selective electrodes

The carbonate-selective electrodes prepared in this work are a typical example of polymer (plastic) membrane-based ion-selective electrodes. They are made by immobilizing carbonate ionophore in a PVC matrix containing a lipophilic salt (TDMACl) and a plasticizer (DOA) to enhance physical and mechanical properties of the membrane [18].

First, ISM was prepared which provides selectivity of the electrode towards the carbonate ions in the measured solution. Generally, the largest component by weight in the ISM is the plasticizer and the mass ratio of PVC to plasticizer (DOA) is 1:2 [6]. The plasticizer acts as a solvent for the ionophore and the additives (TDMACl) within the membrane and improves the mechanical stability of the ISM. It influences both selectivity and sensitivity of the electrode [20]. The composition of the membrane is as follows (Table 5):

Table 5. Ion-selective membrane composition (Carbonate ISE)

| Reagent | Composition (w/w) | Calculated mass (g) | Measured mass (g) |
|-------------------------|-------------------|---------------------|-------------------|
| Carbonate Ionophore VII | 5.10% | 0.0267 | 0.0267 |
| TDMACl | 1.20% | 0.0063 | 0.0063 |
| DOA | 56.80% | 0.2974 | 0.2968 |
| PVC | 36.90% | 0.1932 | 0.1930 |

The ISM components were weighed in a small glass vial and then dissolved in 1.875 ml THF and 1.125 ml Ethyl acetate (5:3 volume ratio). The prepared cocktail was mixed thoroughly using a vortex shaker and then mixed overnight on an orbital shaker platform. Another 0.9 ml THF was added later to fully dissolve the mixture. The THF bottle was purged with Argon gas and closed tightly after every use.

The prepared mixture was shaken well and poured into a small glass ring placed on a glass platform and left for two days allowing the solvents (THF and EtOAc) to evaporate completely. The dried membrane was taken out gently and four disks were punched of 5 mm diameter each and were assembled in Philips IS561 conventional electrode bodies that contain Ag/AgCl wire

(Möller glasbläserei, Zürich, Switzerland). The inner filling solution for conventional carbonate electrodes consists of 0.1 M NaH_2PO_4 , 0.1 M Na_2HPO_4 , and 0.01 M NaCl . The electrodes were pre-conditioned in 0.01 M Na_2CO_3 for a week before first use. While not in use, electrodes were washed thoroughly with DI water and stored in 0.01 M Na_2CO_3 .

4. Results

4.1. Calibration of carbonate-selective electrodes

All the carbonate-selective electrodes were checked against 0.01 M Na₂CO₃ solution (pH = 10.61) and showed very similar response to one another. The electrodes were tapped gently to remove any air bubbles inside the electrode before use. After this, the electrodes were calibrated against prepared standard solutions using Ag | AgCl | 3M KCl | 1M LiOAc as a reference electrode. The average pH of these standard solutions was in the range of 10.4 – 11.2. The potential response (mV) of carbonate ISEs against standard solutions is included in appendix B. The potentiometric response of the electrodes is shown in Fig. 3.

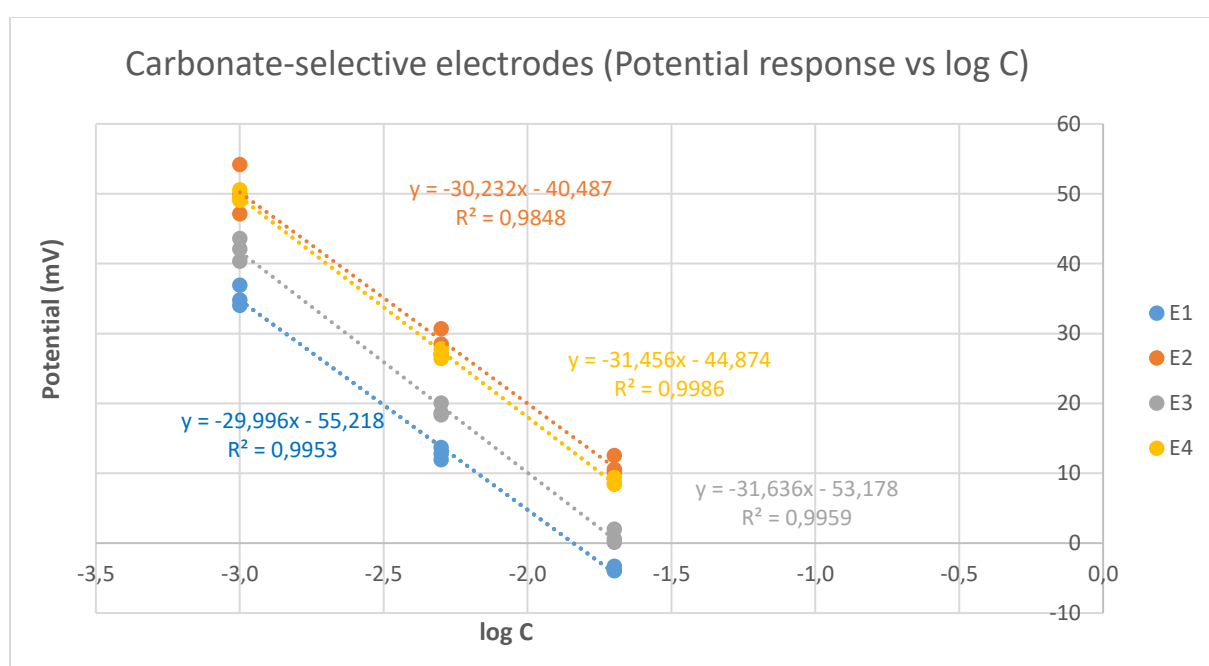


Fig. 3. Potentiometric response of four identical carbonate-selective electrodes (E1-E4) in standard solutions (calibration solutions 1-3 in Table 3).

The calibration graph shows three replicate measurements against each standard solution on the same day by each electrode. The electrodes showed good reproducibility and repeatability. Under ideal conditions, the Nernstian response is -29.1 mV/decade for divalent anions, and the slopes obtained during calibration are close to this value. The linearity of the response given by

the electrodes is also good. The electrodes were used for over 8 months and were able to produce consistently good response in this period.

However, it is important to maintain good storage conditions for standard solutions and change the standard solutions if the carbonate content (potential response value) seems to be changing with time during calibration. This can be due to loss of carbonate in the solutions due to release of CO₂ to the atmosphere over time or increase in carbonate due to uptake of CO₂ from the atmosphere over time. Therefore, it is advisable to check stability of the standard solutions from time to time and replace them if needed.

4.2. Calibration of other ion-selective electrodes

The potassium, sodium and chloride selective electrodes were calibrated using the prepared calibration (standard) solutions and several replicates were made over a period of seven weeks. The calibration graphs along with the respective linear equation and R-squared values, and response change over time (every week) are indicated in the graphs below for each ISE. The residual analysis for each ISE and corresponding potential response values are included in the appendices A and B respectively.

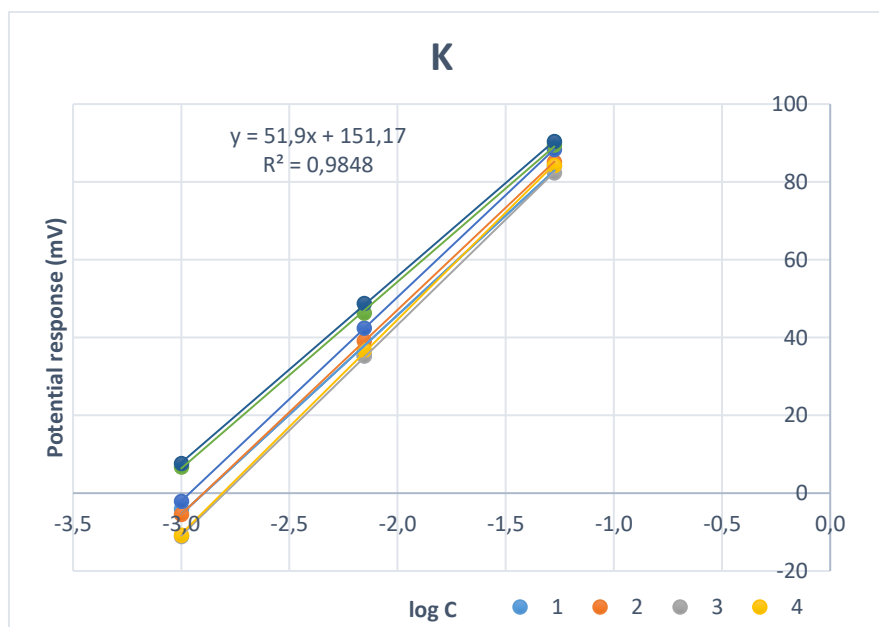


Fig. 5. Potassium ISE potential response change (week 1-7)

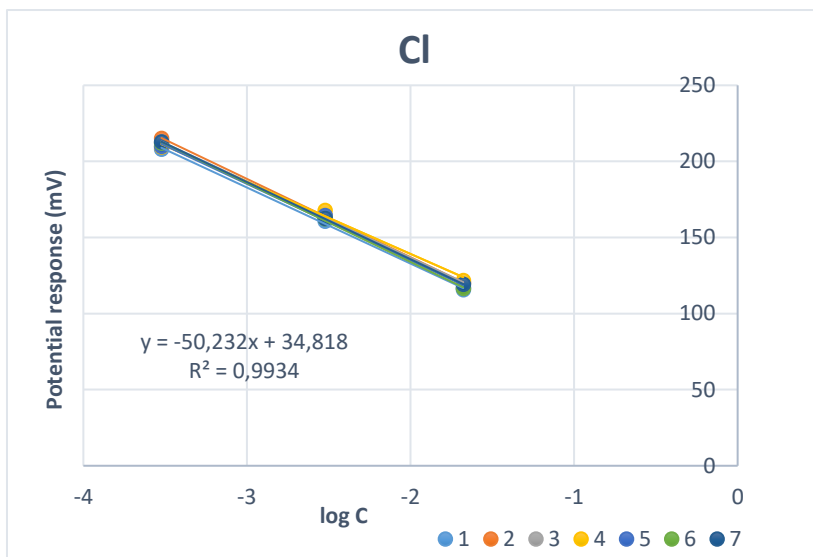


Fig. 6. Chloride ISE potential response change (week 1-7)

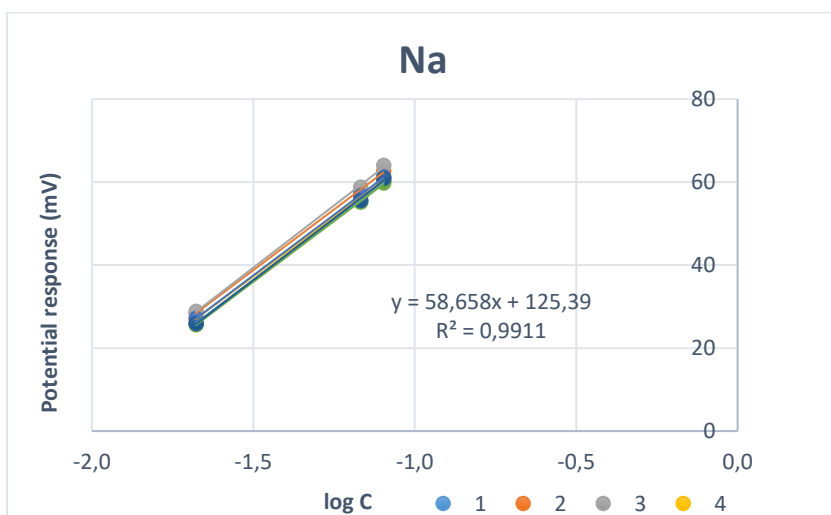


Fig. 7. Sodium ISE potential response change (week 1-7)

As mentioned before, for the ideal “Nernstian response”, the slope obtained for monovalent ions (e.g., K^+ , Na^+ , and Cl^-) should be ± 59.1 mV/decade. The linear response by the ISEs was relatively close to this value. The Na-ISE shows Nernstian response whereas a sub-Nernstian response can be observed for both K-ISE and Cl-ISE. The electrodes deviate from ideal behaviour due to change in several external factors like room temperature, atmospheric pressure conditions, pH, interfering ions, etc.

4.3. Sample measurements

Two ESP ash samples were taken from different pulp and paper mills in Finland and one from Austria. The ash was collected directly from the ash conveyors, right before the ash is mixed with black liquor in the mixing tank to form green liquor.

The samples dissolved immediately in deionized water (DI water). The samples were dissolved according to 1:200 ratio for analysis (e.g., 1 g ash in 200 mL DI water). The samples were analysed using ion-selective electrodes for the respective ions (K^+ , Na^+ , Cl^- , and CO_3^{2-}) and the SO_4^{2-} content was calculated as the rest of the content of the ash (in mass%).

The average results obtained by several replicates ($n = 12$) are summarized in Table 6. The precision values are calculated by calculating the sample standard deviation of three replicate measurements of the same dilution on the same day for 4 days. On each day a fresh sample solution was prepared and measured.

Table 6. Ionic concentrations in samples (% w/w) and sample standard deviation (\pm % w/w)

| | Sample 1 | | Sample 2 | | Sample 3 | | Average Precision |
|-------------|----------|--------------|----------|--------------|----------|--------------|-------------------|
| | % (w/w) | \pm %(w/w) | % (w/w) | \pm %(w/w) | % (w/w) | \pm %(w/w) | \pm %(w/w) |
| K^+ | 4.46 % | 0.63 % | 3.75 % | 0.30 % | 5.00 % | 0.68 % | 0.54 % |
| Cl^- | 0.50 % | 0.13 % | 0.28 % | 0.06 % | 1.17 % | 0.11 % | 0.10 % |
| Na^+ | 29.69 % | 0.57 % | 30.39 % | 1.17 % | 29.25 % | 0.65 % | 0.80 % |
| CO_3^{2-} | 6.13 % | 0.78 % | 10.12 % | 1.01 % | 5.36 % | 0.50 % | 0.77 % |
| SO_4^{2-} | 59.32 % | 0.94 % | 55.72 % | 0.85 % | 59.23 % | 1.01 % | 0.93 % |

The average precision value in the table indicates the average of precision obtained in three different samples using the same ISE.

4.4. pH and conductivity measurements

The pH and conductivity values of the standard solutions and samples were regularly measured using Mettler Toledo S20 SevenEasy pH meter and the Mettler Toledo FiveEasy conductivity meter respectively, and the average recorded values are given in Table 7. The conductivity meter reads electrical conductivity of the solution and can also normalize the reading according to temperature change. The ionic strength of the solutions can roughly be estimated from the electrical conductivity using the relationship [21]:

$$I \text{ (mol/L)} = K \cdot \kappa \text{ (\mu S/cm)} \quad (3)$$

where, $K = 0.000016$; I is the ionic strength and κ is the measured electrical conductivity of the solution.

Table 7. measured pH, conductivity and ionic strength of standard solutions and samples.

| | pH | Conductivity ($\mu\text{S/cm}$) | Ionic strength (mol/L) |
|------------|------|-----------------------------------|------------------------|
| C1 | 11.2 | 6696.7 | 0.107 |
| C2 | 10.9 | 6327.3 | 0.101 |
| C3 | 10.4 | 6939.7 | 0.111 |
| Andritz S1 | 10.9 | 5768.6 | 0.092 |
| Andritz S2 | 11.0 | 5869.4 | 0.094 |
| Andritz S3 | 10.8 | 6019.3 | 0.096 |

The ionic strength of the standard solutions and samples can also be calculated theoretically using equation (4) based on known/ calculated ionic concentration (C_i) and ionic charge (z_i) of each species known to be present in the solution.

$$I = 0.5 \sum z_i^2 \cdot C_i \quad (4)$$

Table 8. Calculated ionic strength of standard and sample solutions

| Solution: | Ionic strength (mol/L) |
|-----------|------------------------|
| C1 | 0.111 |
| C2 | 0.111 |
| C3 | 0.111 |

| | |
|------------|-------|
| Andritz S1 | 0.107 |
| Andritz S2 | 0.110 |
| Andritz S3 | 0.106 |

Here, we can see that the experimental ionic conductivity values agree well with the theoretically calculated ionic conductivity values given in tables 7 and 8 respectively.

4.5. Measurement by reference methods

The standard solutions and samples were tested for amount of Na⁺, K⁺, Cl⁻, and SO₄²⁻ present using ICP-OES and Ion Chromatography. The results are as follows (Table 9):

Table 9. Ionic concentrations using reference methods (ICP-OES for Na⁺, K⁺ and IC for Cl⁻ and SO₄²⁻)

| | K ⁺ (mg/L) | Na ⁺ (mg/L) | SO ₄ ²⁻ (mg/L) | Cl ⁻ (mg/L) |
|------------|-----------------------|------------------------|--------------------------------------|------------------------|
| C1 | 26.8 | 1300.5 | 856.1 | 643.6 |
| C2 | 241.6 | 1108.1 | 3052.4 | 77.8 |
| C3 | 1864.7 | 339.6 | 3624.6 | 11.1 |
| Andritz S1 | 205.5 | 1088.6 | 3165.8 | 22.9 |
| Andritz S2 | 177.4 | 1043.6 | 2871.2 | 15.0 |
| Andritz S3 | 215.1 | 1009.0 | 3098.6 | 32.2 |

The comparison of results obtained by ISE measurements and reference analysis (ICP-OES for Na⁺, K⁺ and IC for Cl⁻ and SO₄²⁻) in mass% are presented in the following table:

Table 10. Comparison of compositions (% w/w) using reference methods with ISE results/ calculated values

| K ⁺ | Reference | ISE/ calculated: | Na ⁺ | Reference | ISE/ calculated: |
|----------------|-----------|------------------|-----------------|-----------|------------------|
| C1 | 0.50 % | 0.82 % | C1 | 24.19 % | 38.46 % |
| C2 | 4.44 % | 5.23 % | C2 | 20.35 % | 29.96 % |
| C3 | 30.38 % | 34.11 % | C3 | 5.53 % | 7.96 % |

| | | | | | |
|-----------------|-----------|------------------|-------------------------------|-----------|-------------|
| Andritz S1 | 3.78 % | 4.45 % | Andritz S1 | 20.03 % | 29.66 % |
| Andritz S2 | 3.29 % | 3.74 % | Andritz S2 | 19.36 % | 30.31 % |
| Andritz S3 | 4.27 % | 5.00 % | Andritz S3 | 20.05 % | 29.25 % |
| Cl ⁻ | Reference | ISE/ calculated: | SO ₄ ²⁻ | Reference | Calculated: |
| C1 | 11.97 % | 15.58 % | C1 | 15.92 % | 20.06 % |
| C2 | 1.43 % | 2.04 % | C2 | 56.04 % | 57.02 % |
| C3 | 0.18 % | 0.18 % | C3 | 59.06 % | 56.77 % |
| Andritz S1 | 0.42 % | 0.50 % | Andritz S1 | 58.24 % | 59.27 % |
| Andritz S2 | 0.28 % | 0.28 % | Andritz S2 | 53.25 % | 55.57 % |
| Andritz S3 | 0.64 % | 1.17 % | Andritz S3 | 61.57 % | 59.22 % |

The samples were also sent to an external laboratory to estimate measurement accuracy. Table 11 compares the mass % (w/w) of different ions in the sample solutions obtained by reference analysis and ISE measurements. The reference method used for each analysis is included in appendix B.

Table 11. Comparison of Reference analyses from external laboratory and ISE measurements

| | | | | | |
|-----------------|-------------|-------------|-------------------------------|------------|--------------|
| K ⁺ | Reference | ISE: | Na ⁺ | Reference | ISE: |
| Andritz S1 | 4.3±0.6 % | 4.46±0.63 % | Andritz S1 | 28.0±4.2 % | 29.69±0.57 % |
| Andritz S2 | 3.9±0.5 % | 3.75±0.30 % | Andritz S2 | 29.0±4.4 % | 30.39±1.17 % |
| Andritz S3 | 5.1±0.7 % | 5.00±0.68 % | Andritz S3 | 27.0±4.1 % | 29.25±0.65 % |
| Cl ⁻ | Reference | ISE: | SO ₄ ²⁻ | Reference | Calculated: |
| Andritz S1 | 0.52±0.05 % | 0.50±0.13 % | Andritz S1 | 58.0±5.8 % | 59.32±0.94 % |
| Andritz S2 | 0.32±0.03 % | 0.28±0.06 % | Andritz S2 | 55.0±5.5 % | 55.72±0.85 % |
| Andritz S3 | 0.85±0.09 % | 1.17±0.11 % | Andritz S3 | 58.0±5.8 % | 59.23±1.01 % |

| | | |
|-------------------------------|-----------|--------------|
| CO ₃ ²⁻ | Reference | ISE: |
| Andritz S1 | 5.3±0.8 % | 6.13±0.78 % |
| Andritz S2 | 8.7±1.3 % | 10.12±1.01 % |
| Andritz S3 | 3.2±0.5 % | 5.36±0.85 % |

The comparison shows good agreement of ISE measurements with the results from the external laboratory, especially for ionic concentrations of Na^+ , K^+ , Cl^- , and SO_4^{2-} ions in the samples. The CO_3^{2-} concentration is systematically higher than the reference analysis which is due to huge dependency of CO_3^{2-} on the pH at which it is determined by the ISE.

4.6. Measurement uncertainty

In the table 11, reference analysis results and ISE measurements are given with their respective uncertainty estimates. The reference analysis uncertainty was given by the external laboratory as $\text{Na}^+ : \pm 15\%$; $\text{K}^+ : \pm 13\%$; $\text{Cl}^- : \pm 10\%$; $\text{CO}_3^{2-} : \pm 15\%$ and $\text{SO}_4^{2-} : \pm 10\%$ respectively. The uncertainty value of the ISE measurements is presented as the long-term reproducibility of the respective ionic concentrations. This means the same sample was analyzed for several days, three times from the same dilution on same day and fresh dilution was prepared every day. The precision was calculated as sample standard deviation value of these replicate measurements done over time. The uncertainty source therefore includes sub-sampling of the ash samples received and dilution made each time. Other sources of uncertainty include temperature differences during measurements, filling of volumetric flask during dilution, weighing etc.

5. Practicalities:

1. All electrodes should be operated below 40°C. It is also reasonable to maintain standards and sample around same temperature, preferably at ambient temperature.
2. Electrodes should not be let dry and should always be held in an upright position.
3. The reference electrode should be checked for inner filling solution from time to time, and the porous plug should be checked for blockage; the air valves (inner filling and outer filling) should be open while the reference electrode is in use to allow KCl leakage.
4. Commercial electrodes work well in the pH range of 2-12. ESP ash samples when diluted in a 1:200 ratio, have a pH around 11, which is suitable for analysis with ISE's.
5. Before the first use, commercial ISEs might need to be pre-conditioned in their respective conditioning solutions. The respective recommended time and pre-conditioning solution is given in the operating instructions manual.
6. When not in use, they should be stored in the same conditioning solution or stored dry as per the electrode specific instructions on the manual.
7. In case of sluggish response, it is suggested to check membrane surface for any deposition and clean it with DI water and then condition the electrodes for a few hours.
8. In case of erratic measurement values, first check the electrode membrane surface for bubbles, and gently tap the electrodes. It can also be washed with DI water and wiped gently, without touching the membrane surface and check again. If the problem persists, consider refilling the inner filling solution that comes along with the package and condition it for a few hours before using again.

6. Conclusion

From the results obtained in section 4.1 and 4.2, we can see that measurements using ion-selective electrodes depend largely upon the stability of the calibration curve. The same standard potential value (intercept) or slope cannot be used for calculation of analyte concentration over a longer period due to the drift of response measured by the same ISE for the same standard solutions with time. This suggests that the ISEs must be regularly calibrated to avoid the measurement error due to potential response drift.

The ionic concentrations were calculated for three different samples using the potential response given by millivoltmeter for respective ISEs and slope and intercept values given by the calibration curve obtained on the same day. These samples were taken from different pulp and paper mills in Finland and abroad. These values are presented in section 4.3, and they fall well within the range of expected concentrations in the ash samples (given in section 3.4).

The standard deviation of the ionic concentrations in different samples was also calculated which gives intermediate precision of sample measurements by ISEs. The average precision was calculated taking average of precision values obtained for the three different samples analysed to demonstrate reliability of ISE measurements. From table 6 we can observe average precision to be <1 % for each ionic concentration (in %w/w).

In section 4.4, pH measurements and electrical conductivity measurements for standard solutions and samples are given. It is important to make these measurements since the ionic activity strongly depends upon pH and ionic strength of the solution. Therefore, these measurements were made to establish that the standard solutions used for calibration curve and samples analysed have similar ionic activity during the analysis. It is also possible to calculate theoretical ionic strength using the relation between ionic concentration and charge of the ion using equation 4. The pH meter and conductivity meter should be calibrated regularly using the application guide for accurate measurements [22].

At last, reference analysis was done to check accuracy of the ISE measurements and to prove suitability of the method for the desired process analysis. Table 10 and 11 compare the ISE measurement results with reference analysis for this purpose. The thesis work concludes ISEs can be used for determination of ionic concentrations of Na^+ , K^+ , Cl^- , and CO_3^{2-} and then SO_4^{2-} concentration can be calculated as rest of dry solid (w/w mass %). It is important to maintain good storage condition for the standard solutions and prepare fresh standard solution if there is deviation from the Nernstian response or poor linearity of the calibration curve.

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Appendix -A

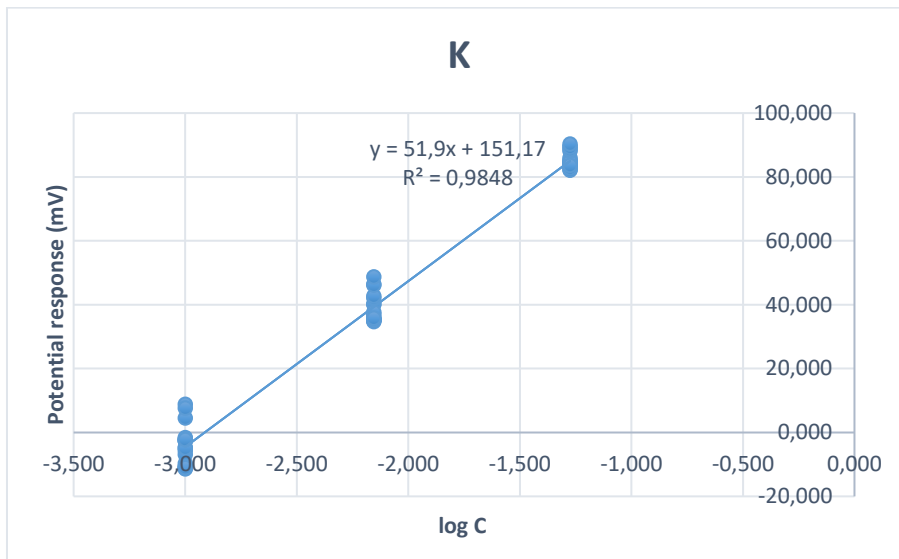


Fig. 8. Potassium ISE calibration curve

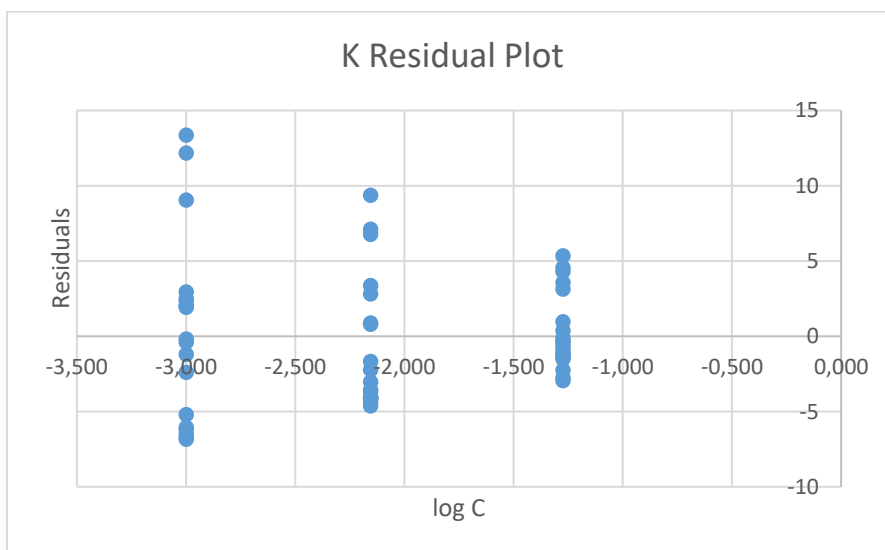


Fig 9. Residual analysis of Potassium ISE calibration curve

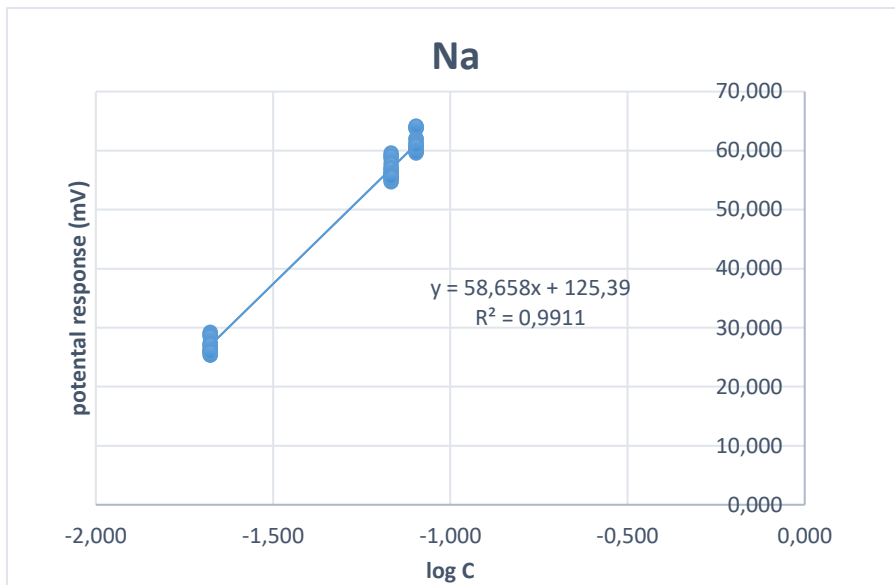


Fig. 10. Sodium ISE calibration curve

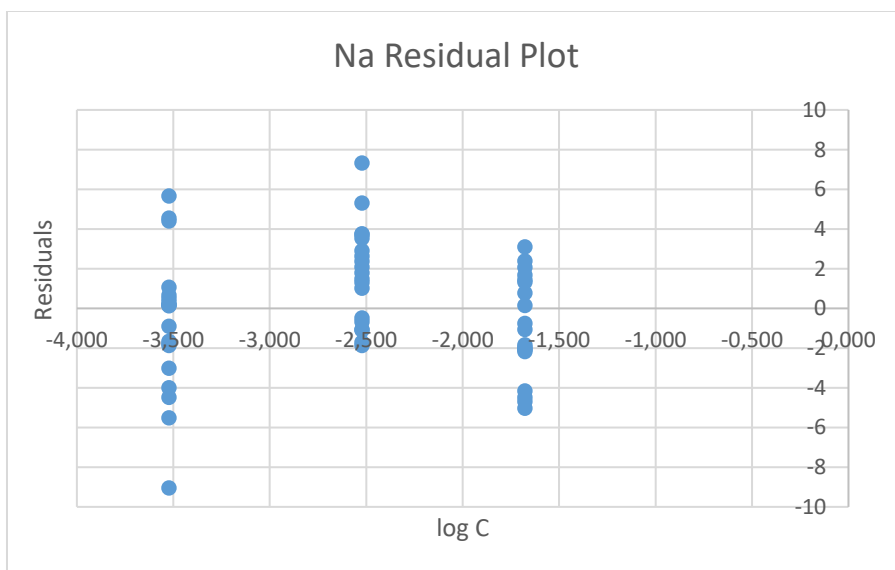


Fig 11. Residual analysis of Sodium ISE calibration curve

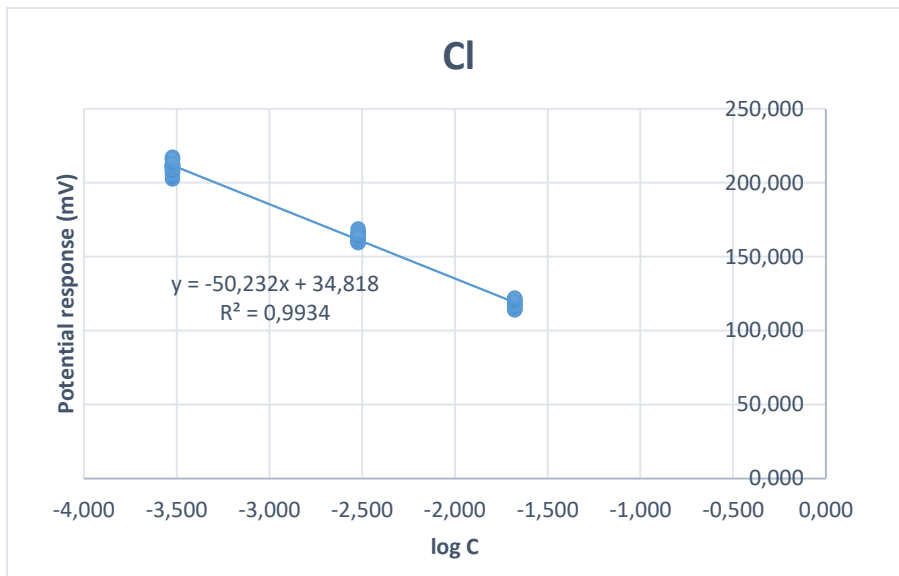


Fig.12. Chloride ISE calibration curve

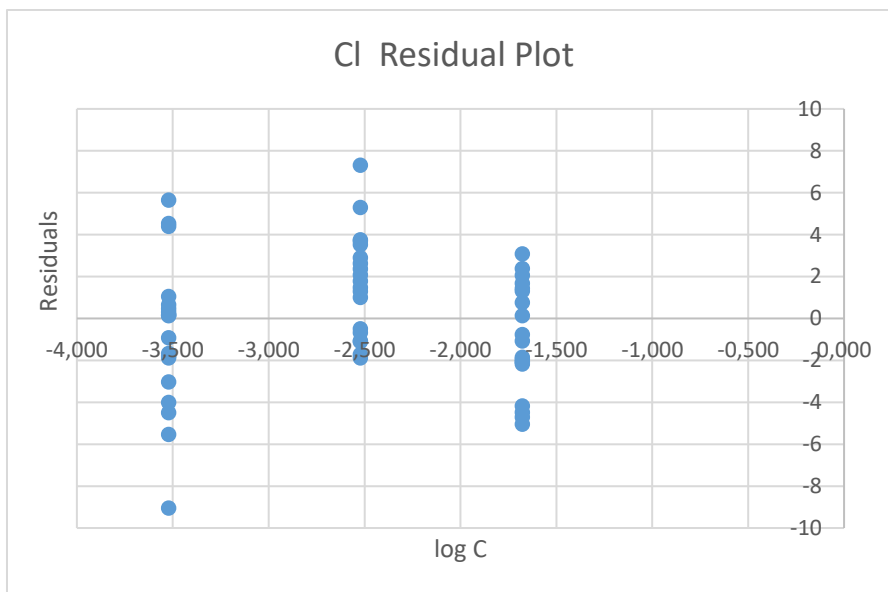


Fig 13. Residual analysis of Chloride ISE calibration curve

Appendix -B

Table 12. Carbonate ISEs (E1,E2,E3,E4) potential response (mV) against standard solutions

| Replicates | Standard | log C (CO ₃ ²⁻) | E1 | E2 | E3 | E4 |
|------------|----------|--|---------|---------|---------|---------|
| 1 | C1 | -1,699 | -3,9641 | 10,1025 | 0,1152 | 8,3978 |
| | C2 | -2,301 | 12,7615 | 27,0398 | 18,3500 | 26,4002 |
| | C3 | -3,000 | 34,0147 | 47,1254 | 40,3532 | 49,0524 |
| 2 | C1 | -1,699 | -3,8663 | 10,5663 | 0,595 | 8,6583 |
| | C2 | -2,301 | 13,6955 | 28,4524 | 18,6391 | 27,0106 |
| | C3 | -3,000 | 34,8194 | 49,8314 | 42,0679 | 50,5336 |
| 3 | C1 | -1,699 | -3,303 | 12,535 | 1,9808 | 9,3617 |
| | C2 | -2,301 | 11,9187 | 30,6751 | 20,041 | 27,7801 |
| | C3 | -3,000 | 36,8841 | 54,1659 | 43,6123 | 49,5066 |

Table 13. ISE's potential response (mV) against standard solutions

| | Replicates | Standard | log C (K ⁺) | Potential response (K ⁺) | Log C (Cl ⁻) | Potential response (Cl ⁻) | Log C (Na ⁺) | Potential response (Na ⁺) | |
|--------|------------|----------|-------------------------|--------------------------------------|--------------------------|---------------------------------------|--------------------------|---------------------------------------|--------|
| Week 1 | 1 | C1 | -3,000 | -9,739 | -1,678 | 114,613 | -1,097 | 59,940 | |
| | | C2 | -2,155 | 35,297 | -2,523 | 160,873 | -1,167 | 55,666 | |
| | | C3 | -1,275 | 83,488 | -3,523 | 212,441 | -1,678 | 26,102 | |
| | 2 | C1 | -3,000 | -5,742 | -1,678 | 117,149 | -1,097 | 60,185 | |
| | | C2 | -2,155 | 34,967 | -2,523 | 160,442 | -1,167 | 55,960 | |
| | | C3 | -1,275 | 83,679 | -3,523 | 210,867 | -1,678 | 25,872 | |
| | 3 | C1 | -3,000 | -2,610 | -1,678 | 117,253 | -1,097 | 59,813 | |
| | | C2 | -2,155 | 34,697 | -2,523 | 162,847 | -1,167 | 54,723 | |
| | | C3 | -1,275 | 83,834 | -3,523 | 208,760 | -1,678 | 25,399 | |
| | 4 | C1 | -3,000 | -2,478 | -1,678 | 117,050 | -1,097 | 59,977 | |
| | | C2 | -2,155 | 35,204 | -2,523 | 159,841 | -1,167 | 55,632 | |
| | | C3 | -1,275 | 84,314 | -3,523 | 207,783 | -1,678 | 26,227 | |
| | 5 | C1 | -3,000 | -2,551 | -1,678 | 114,393 | -1,097 | 60,522 | |
| | | C2 | -2,155 | 35,624 | -2,523 | 159,669 | -1,167 | 55,587 | |
| | | C3 | -1,275 | 84,564 | -3,523 | 206,256 | -1,678 | 26,408 | |
| | 6 | C1 | -3,000 | -1,592 | -1,678 | 114,059 | -1,097 | 60,578 | |
| | | C2 | -2,155 | 36,288 | -2,523 | 161,057 | -1,167 | 55,896 | |
| | | C3 | -1,275 | 84,716 | -3,523 | 202,728 | -1,678 | 26,049 | |
| | Week 2 | 1 | C1 | -3,000 | -6,930 | -1,678 | 120,530 | -1,097 | 62,050 |
| | | | C2 | -2,155 | 37,098 | -2,523 | 163,620 | -1,167 | 56,030 |
| | | | C3 | -1,275 | 84,067 | -3,523 | 217,435 | -1,678 | 27,431 |
| | | 2 | C1 | -3,000 | -4,715 | -1,678 | 119,862 | -1,097 | 62,025 |

| | | | | | | | | |
|--------|---|----|--------|---------|--------|---------|--------|--------|
| | | C2 | -2,155 | 40,111 | -2,523 | 164,178 | -1,167 | 58,649 |
| | | C3 | -1,275 | 85,364 | -3,523 | 211,962 | -1,678 | 28,641 |
| | | C1 | -3,000 | -4,921 | -1,678 | 120,409 | -1,097 | 63,791 |
| | 3 | C2 | -2,155 | 40,214 | -2,523 | 165,302 | -1,167 | 59,164 |
| | | C3 | -1,275 | 85,964 | -3,523 | 216,320 | -1,678 | 29,224 |
| | | C1 | -3,000 | -10,726 | -1,678 | 121,154 | -1,097 | 63,804 |
| Week 3 | 1 | C2 | -2,155 | 35,256 | -2,523 | 163,031 | -1,167 | 59,591 |
| | | C3 | -1,275 | 82,247 | -3,523 | 216,177 | -1,678 | 29,030 |
| | | C1 | -3,000 | -11,384 | -1,678 | 120,778 | -1,097 | 64,033 |
| | 2 | C2 | -2,155 | 35,134 | -2,523 | 163,330 | -1,167 | 59,070 |
| | | C3 | -1,275 | 82,041 | -3,523 | 209,902 | -1,678 | 28,855 |
| | | C1 | -3,000 | -11,250 | -1,678 | 118,334 | -1,097 | 64,190 |
| | 3 | C2 | -2,155 | 35,258 | -2,523 | 165,250 | -1,167 | 57,770 |
| | | C3 | -1,275 | 82,752 | -3,523 | 211,932 | -1,678 | 28,541 |
| | | C1 | -3,000 | -10,587 | -1,678 | 121,479 | -1,097 | 60,016 |
| Week 4 | 1 | C2 | -2,155 | 37,663 | -2,523 | 168,870 | -1,167 | 57,087 |
| | | C3 | -1,275 | 84,857 | -3,523 | 211,911 | -1,678 | 27,121 |
| | | C1 | -3,000 | -11,050 | -1,678 | 122,187 | -1,097 | 60,275 |
| | 2 | C2 | -2,155 | 35,784 | -2,523 | 166,845 | -1,167 | 56,257 |
| | | C3 | -1,275 | 83,558 | -3,523 | 207,291 | -1,678 | 26,855 |
| | | C1 | -3,000 | -2,042 | -1,678 | 116,921 | -1,097 | 61,221 |
| Week 5 | 1 | C2 | -2,155 | 42,135 | -2,523 | 165,081 | -1,167 | 56,629 |
| | | C3 | -1,275 | 88,133 | -3,523 | 209,995 | -1,678 | 27,093 |
| | | C1 | -3,000 | -2,175 | -1,678 | 117,011 | -1,097 | 61,248 |
| | 2 | C2 | -2,155 | 42,690 | -2,523 | 163,912 | -1,167 | 57,000 |
| | | C3 | -1,275 | 88,563 | -3,523 | 210,120 | -1,678 | 27,191 |
| | | C1 | -3,000 | 8,829 | -1,678 | 114,929 | -1,097 | 59,930 |
| Week 6 | 1 | C2 | -2,155 | 46,433 | -2,523 | 160,483 | -1,167 | 55,133 |
| | | C3 | -1,275 | 89,566 | -3,523 | 212,254 | -1,678 | 25,807 |
| | | C1 | -3,000 | 4,508 | -1,678 | 118,023 | -1,097 | 59,591 |
| | 2 | C2 | -2,155 | 46,108 | -2,523 | 164,454 | -1,167 | 55,174 |
| | | C3 | -1,275 | 89,301 | -3,523 | 212,085 | -1,678 | 25,381 |
| | | C1 | -3,000 | 7,631 | -1,678 | 119,236 | -1,097 | 60,868 |
| Week 7 | 1 | C2 | -2,155 | 48,701 | -2,523 | 162,560 | -1,167 | 55,558 |
| | | C3 | -1,275 | 90,341 | -3,523 | 212,840 | -1,678 | 25,894 |
| | | C1 | -3,000 | | | | | |

Table 14. Standard methods used in laboratory for reference analysis of ESH ash samples.

| Ion | Method |
|-------------------------------|---|
| Na ⁺ | Laboratory Internal method: Sample is dissolved in HNO ₃ , determination by atomic absorption spectrometry (AAS) |
| K ⁺ | Laboratory Internal method: Sample is dissolved in HNO ₃ , determination by atomic absorption spectrometry (AAS) |
| Cl ⁻ | Laboratory Internal method: Sample is dissolved in HNO ₃ , determination by potentiometric titration with AgNO ₃ solution |
| SO ₄ ²⁻ | SCAN-N 6:64 (modified): Sample is dissolved in water, Sulphate ions are determined gravimetrically by precipitating with BaCl ₂ . |
| CO ₃ ²⁻ | SCAN-N 32:98: Carbonates are liberated in a reactor flask containing HCl; CO ₂ is absorbed into NaOH solution; Change in the electrical conductivity of NaOH solution is measured. |