

Sulfur compounds in white and green liquor

Comparison of analytical methods for the determination of reduction degree

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Analysis of sulfur compounds in the wood pulping industry

The forest industry is one of the biggest exporters and employers in Sweden. One important process in this industry is the Kraft process, which is used in wood pulping to produce paper and cardboard. An integral part of this process is the recycling of the chemicals that the wood chips are cooked in. This mixture, called white liquor, contains sodium hydroxide and -sulfide. The focus of this project was to determine the amount of sulfide and other sulfur compounds throughout the recovery cycle. After use, the white liquor becomes black liquor, which is burned in the recovery boiler. In this step, most of the sulfur is reduced back to sulfide, the active form sulfur in white liquor. The inorganic chemicals from the recovery boiler are then dissolved and become green liquor.

Due to the nature of sulfur in this process, it is important to analyze white and green liquor frequently to ensure that a sufficient amount of sulfur is reduced to sulfide, so that when the new white liquor is used for cooking, the process keeps running efficiently. The current analytical method for the determination of reduction degree (the fraction of sulfide out of the total amount of sulfur) is two potentiometric titrations, with silver nitrate for the determination of sulfide and with lead perchlorate for total sulfur. The latter solution is harmful if swallowed, reproductively toxic, and very toxic to aquatic life with long term effects, which is why there is a demand to replace this method with one that uses no or less harmful chemicals. The alternative being studied in this project is a thermometric titration with barium acetate, which, instead of electric potential, measures changes in temperature due to a heat-releasing reaction with sulfate (the oxidized form of sulfur). The main aim of this project was to determine if the thermometric titration would be an adequate replacement for the current total sulfur method. The comparison was done by using a formaldehyde method similar to the total sulfur method, which gives the sulfate content, making it easier to compare with the thermometric titration results. The reduction degrees calculated through the different methods were also compared. The sulfate content of green liquor is also analyzed by an automatic online recovery liquor analyzer, Alkali R, which measures a titration with barium chloride to reach an optical inflection point. The second aim of this project was to investigate the level and reasons for the discrepancies between the analyzer and laboratory results.

The experimental work of the project had three main parts: Validation of the formaldehyde method and thermometric titration with standard solutions, method comparison with white and green liquor samples, and green liquor comparison with samples directly from Alkali R.

The formaldehyde method was very accurate when using standard solutions of sodium sulfate, but when liquor samples were analyzed, the results were inconsistent. When the thermometric titration was compared to Alkali R, however, the results were statistically equivalent, which would imply that the proposed method is reliable. By comparing the total sulfur content between all tried methods, it was concluded that the discrepancy between the current method and Alkali R are caused by other sulfur compounds in the liquor that aren't accounted for in the Alkali R method.

Abstract

Introduction: The forest industry might not be the first thing to come to mind when thinking of chemistry, but the analysis of cooking chemicals in wood pulping involves many laboratory methods.

Background: The chemical recovery cycle is an integral part of the Kraft process, which makes laboratory analyses of different steps of the process necessary. In the recovery boiler, sulfur is reduced to sulfide, a main active ion in the process. The inorganic chemical mixture is dissolved in white wash, and the resulting green liquor can be analyzed. Many methods use harmful chemicals, like lead perchlorate, which has led to a demand for alternatives.

Aims: Comparing the current method for the determination of reduction degree in white and green liquor with a thermometric titration, as well as investigating the discrepancies between an online recovery analyzer and the laboratory method.

Methods: The current total sulfur method includes two potentiometric titrations, one with silver nitrate to determine the sulfide content, and another with lead perchlorate for the total sulfur content. An adjacent method with formaldehyde was used to yield the sulfate content, for easier comparison with the alternative method. Green liquor results were also compared with the online recovery analyzer, which uses an ABC titration and an optical titration. Samples were collected and analyzed using all described methods for approximately 4 weeks.

Results: Inconsistent results from the formaldehyde method indicate that it isn't a reliable reference point for sulfate content comparison. The adequacy of the new method was therefore investigated by comparing the reduction degrees with the current method and Alkali R, which showed that the thermometric titration is very closely equivalent to the Alkali R, while the total sulfur deviates somewhat consistently from both. This indicates the occurrence of sulfur compounds other than sulfide and sulfate.

Conclusion: The thermometric titration is statistically equivalent to Alkali R which makes it adequate to replace the current method. To still track the other sulfur compounds, the total sulfur titration can be performed less frequently.

Keywords: green liquor, kraft process, method comparison, reduction degree, thermometric titration

Acknowledgement

I would like to thank Billerud Karlsborg for allowing me to conduct this project at the paper mill. Special thanks to my supervisors Ola Nilsson and Kaarina Vallgren for the support throughout the project, especially for quickly helping with new ideas when initial plans didn't work out. Also, thanks to other laboratory personnel for the amazing cooperation when sharing laboratory equipment.

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1 List of abbreviations

EP = End point (of a titration)

LOA = Limit of agreement

LOD = Limit of detection

LOQ = Limit of quantification

Na₂S = Sodium sulfide

Na₂SO₄ = Sodium sulfate

NaOH = Sodium hydroxide

RD = Raw data

S = Sulfur

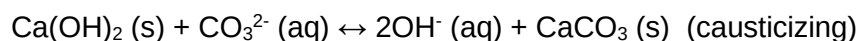
2 Introduction

Forests cover 70% of Sweden's land area. It is therefore no wonder that the forest industry is, and has been for a long time, one of the most important industries in the country. The forest industry accounts for 9-12% of the Swedish industry's total employment, exports, turnover and value added, it has an export value of about 184 billion Swedish crowns (about 16 billion euros), and it employs about 120 000 people [1].

Two very important subsections of the forest industry are the wood pulping industry and paper manufacturing. In order to deeper understand these processes, we must understand the chemical composition of wood. It consists of cellulose, hemicelluloses, lignin and extractives. Lignin acts as an adhesive that holds the cellulose fibers together, and therefore its removal is necessary to free the fibers during wood pulping. Bark is removed before chipping and cooking due to the lack of usable fibers, mostly due to their small size [2].

Wood pulping can be broadly categorized into two categories, mechanical and chemical pulping. The latter category includes the Kraft process, which represents 80% of current pulp production worldwide [3]. It is also the process in use at Billerud Karlsborg, where this project was conducted. The Kraft process was invented in 1879 by Carl Dahl, and entails cooking the wood chips in a solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), so-called white liquor, at a $\text{pH} > 12$, at 160-180 °C and at about 800 kPa steam pressure for 0,5-3 hours. This process gives stronger pulp compared to earlier processes due to faster delignification and therefore less time for carbohydrate degradation [2].

An integral part of the Kraft process is the chemical recovery cycle. After the wood chips are cooked, the resulting black liquor, with dissolved lignin and some other organic compounds, is separated from the cellulose fibers (pulp). At this stage, the weak black liquor has a 15-20% dry solids content, and must be heated to evaporate most of the water in order to increase the black liquor's heating value. At a 70-80% dry solids content, the black liquor can be combusted in the recovery boiler. The main purposes of the recovery boiler are to burn the organic compounds to generate high pressure steam that can be used as a power source in the mill, and to recover the inorganic chemicals as so-called smelt. Sodium and sulfur are recovered as sodium carbonate and sodium sulfide. It is crucial that the recovery boiler is divided into oxygen-rich and oxygen-deficient parts, to ensure efficient combustion of the organic material and to avoid reoxidation of sodium sulfide to sodium sulfate, respectively. The smelt is then dissolved in weak white wash (diluted white liquor from the lime mud wash), which results in a mixture known as green liquor. Green liquor consists mostly of the cations sodium (Na^+) and potassium (K^+) and the anions carbonate (CO_3^{2-}), sulfide (S^{2-}) and hydroxide (OH^-). Chloride (Cl^-), sulfate (SO_4^{2-}) and thiosulfate ($\text{S}_2\text{O}_3^{2-}$), as well as some solid material (green liquor dreg), may also be present in small quantities. The dreg is separated through filtration or sedimentation. The next step is called causticizing, where quicklime (calcium oxide, CaO) is added to the green liquor and the following reactions occur:



This produces hydroxide ions, one of the main active ions in white liquor. The second active ions, sulfide ions, which were recovered in the recovery boiler, remain unchanged in this process. In order to reuse the lime mud (calcium carbonate, CaCO_3), a new cycle is created, where it is separated from the white liquor through filtration, washed with water (which creates the previously mentioned white wash) and then heated to decompose the calcium carbonate according to the following reaction:



This cycle adjacent to the larger chemical recovery cycle is often referred to as the lime cycle. The new white liquor is clarified by settling, where lime mud settles on the bottom of a tank, and thereby closing the chemical recovery cycle. [3]

As mentioned, sulfide ions are one of the two main active ions in the Kraft cooking process, and therefore the sulfide content in white and green liquor must be analyzed, to make sure that the process keeps running as it's supposed to. These results are often presented as the reduction degree or –efficiency, which can have slightly differing definitions. This difference can even be seen within the same book, *Chemical Recovery in the Alkaline Pulping Processes*, where Grace [4] defines it as the ratio of sulfide to sulfide plus sulfate, but Cornell [5] instead defines it as the ratio of sulfide to not only sulfide and sulfate, but also other soda sulfur compounds. This can result in different values for total sulfur for the same sample when using different methods, and therefore yield different values for the reduction degree.

The method currently in use at Billerud Karlsborg analyzes the reduction degree in white and green liquor by measuring the sulfide content through a potentiometric titration with silver nitrate, and the total amount of sulfur by first oxidizing all sulfur compounds to sulfate, which are then measured through a potentiometric titration with lead perchlorate. It therefore uses the latter definition when calculating the reduction degree. The main downside of this “total sulfur method” is the use of lead perchlorate, which is harmful if swallowed, reproductively toxic, and very toxic to aquatic life with long term effects [6].

In an alternative method, a thermometric titration, an excess of barium acetate is added to the sample which leads to the exothermic formation of barium sulfate. After cooling, the remaining barium ions are titrated with sulfuric acid and the temperature change is monitored to conclude the sample's original sulfate content.

To be able to compare sulfate content results directly, a method adjacent to the total sulfur method was also used (which will be called “the formaldehyde method” in this report). The titration part of the procedure is the same, but formaldehyde and acetone are added to the sample in order to measure just the sulfate content. This is possible because the formaldehyde

masks other interfering sulfur compounds. The role of the acetone is to reduce the solubility of the lead sulfate being formed.

An online recovery liquor analyzer, Alkali R, measures the sulfide content through an ABC-titration and the sulfate content by reaching an optical inflection point through the addition of barium chloride. It therefore calculates the reduction degree as sulfide to sulfide plus sulfate. Some discrepancies between the online measurements and laboratory results have been observed. Samples were taken directly from the analyzer for the comparison to be as accurate as possible.

The two aims of this project are therefore:

- To determine if the proposed thermometric titration is an adequate replacement for the current total sulfur method for the determination of reduction degree in white and green liquor.
- To investigate why there are discrepancies between the laboratory results and the automatic online recovery liquor analyzer Alkali R.

3 Materials and methods

3.1 Chemicals

All chemicals used and stock solutions prepared are described below.

3.1.1 Method validation

Sodium sulfate anhydrous granulated for organic trace analysis. Merck Life Science UK. Sodium sulfate stock solutions were prepared by igniting a portion of the anhydrous salt at 550°C in a crucible, weighing the amount needed with a four decimal precision, and filling up with deionized water to the mark in a volumetric flask.

3.1.2 The total sulfur method

Silver nitrate solution for 1000 ml (Titrisol ampoule). 0,1 M. Merck Life Science AB.

Sodium hydroxide, 1M. LabService AB.

Ammonia solution 25%. AnalaR NORMAPUR analytical reagent. VWR International AB.

Alkaline sodium sulfite solution (approximately 0,5 M sodium sulfite) made by dissolving 60 g sodium sulfite (Pro analysi EMSURE reag. Ph Eur. Sigma-Aldrich Sweden AB.) and 40 g sodium hydroxide (pro analysi EMSURE. Sigma-Aldrich Sweden AB.) in 1000 ml of water.

Hydrogen peroxide 30%. Pro analysi EMSURE ISO. Merck Life Science AB.

Cobalt(II) nitrate hexahydrate. Pro analysi EMSURE. Merck Life Science AB. 5 mM solution made by dissolving 0,145 g in 100 ml deionized water.

Ethanol 99,5%. A-sprit. KiiltoClean.

Perchloric acid 70-72%. Pro analysi EMSURE ACS, ISO, Reag. Ph Eur. Merck Life Science AB. 1 M solution made by diluting 40 ml of the concentrate acid to 500 ml of deionized water.

Lead(II) perchlorate trihydrate. Thermo Fisher. 50 mM solution made by dissolving 46 g in 2000 ml of deionized water.

Sodium sulfate anhydrous granulated for organic trace analysis. Merck Life Science UK. 50 mM solution made by drying the salt at 105 °C and dissolving 7,10 g in 1000 ml of deionized water.

3.1.3 The formaldehyde method

Acetone. Pro analysi EMSURE ACS, ISO, Reag. Ph Eur. Merck Life Science AB.

Formaldehyde solution about 37% GR for analysis stabilized with about 10% methanol. ACS, Reag. Ph Eur. Merck Life Science AB.

Perchloric acid 70-72%. Pro analysi EMSURE ACS, ISO, Reag. Ph Eur. Merck Life Science AB. 1 M solution made by diluting 40 ml of the concentrate acid to 500 ml of deionized water.

Lead(II) perchlorate trihydrate. Thermo Fisher. 50 mM solution made by dissolving 46 g in 2000 ml of deionized water.

3.1.4 Thermometric titration

Titrant: 1M sulfuric acid. LabService AB.

Acid mixture: 3,4 M hydrochloric acid and 0,17 M barium acetate. LabService AB.

3.1.5 Alkali R

1 M hydrochloric acid solution. AVS TITRINORM Reag. Ph. Eur., Reag. USP, NF volumetric solution. VWR Chemicals.

2-propanol. Puriss. Labservice AB.

0,025 M barium chloride solution. Labservice AB.

3.2 Equipment

3.2.1 The total sulfur and formaldehyde methods

All: 814 USB Sample Processor, 802 Stirrer, 800 Dosino (all automatically dispensed chemicals), tiamo (control and database). Metrohm.

Sulfide: 836 Titrand (AgNO₃), Ag Titrode (6.00430.100), 685 Dosimat (NaOH, NH₃). Metrohm.

Total sulfur and formaldehyde: 809 Titrand (PbClO₄), Pb ion-selective electrode (6.0502.170), Ecotrode plus (6.0262.100), 685 Dosimat (ethanol). Metrohm.

3.2.2 Thermometric titration

859 Titrotherm, 804 Ti Stand, 802 Stirrer, Thermoprobe (6.9011.020), tiamo (control and database). Metrohm.

3.2.3 Alkali R

Valmet recovery liquor analyzer (Alkali R).

3.3 Methods

3.3.1 Method validation

The thermometric titration and the formaldehyde method were performed according to the below descriptions and validated based on the following criteria.

Limit of detection and quantification: 11 measurements were performed with a 0,10 g SO₄²⁻/l stock solution for the formaldehyde method and with blank samples (deionized water) for the thermometric titration. The standard deviations were calculated. LOD was defined as 3 times the standard deviation and LOQ as 10 times the standard deviation.

Linear range: A measurement range was chosen based on previous calculated results of sulfate content in green liquor, and 6 points were chosen equally spread across this range. 5 replicates of stock solutions at each concentration (1, 3, 6, 9, 12 and 15 g SO₄²⁻/l) were measured and their averages were plotted.

Trueness and precision: Two concentration points were chosen, one in the lower and one in the higher end of the determined linear range for the thermometric titration. 11 replicates were measured of each concentration (2 and 5 g SO₄²⁻/l) and the standard deviations, relative standard deviations, biases and relative biases were calculated.

The standard deviations were calculated using the formula

$$s = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}}$$

where x is each measurement point, $\bar{x}$ is their mean and n is the number of measurement points.

The relative standard deviations were calculated through $\frac{s}{\bar{x}} \times 100$.

The biases were calculated through $\bar{x} - x_{ref}$ and the relative biases through $\frac{\bar{x} - x_{ref}}{x_{ref}} \times 100$, where x_{ref} is the stock solution concentration.

The validation criteria and number of measurements were based on validation procedures at Billerud Karlsborg, and supported by the Eurachem method validation guide [7].

3.3.2 Method comparison

Samples of white and green liquor were taken from the regular sample collection points for 10 days and analyzed by all below described analytical methods and the results were compared by using Bland-Altman plots and paired t-tests. Bland-Altman plots show the average result of the two methods on the x-axis and the difference between the results in the y-axis, which shows if there's any correlation between the concentrations and deviations. The bias (mean deviation) and the upper and lower limits of agreement (LOA) were also plotted. The LOAs are calculated using the formula

$$LOA = \bar{x} \pm T \times s$$

where $\bar{x}$ is the mean deviation, T is the critical t-value for a two tailed t-test for a significance level of 0,05 (depends on number of freedom degrees) and s is the standard deviation of the differences. Addition is used for the upper LOA and subtraction for the lower LOA. These lines give the 95% confidence interval.

The paired t-test calculates the t-value using the formula

$$t - value = |\bar{x}| \times \frac{\sqrt{n}}{s}$$

where $|\bar{x}|$ is the absolute value of the mean difference, n is the number of measurement points and s is the standard deviation of the differences.

Samples were also collected directly from Alkali R and analyzed for 10 days. These results were added to the method comparison.

The samples were always cooled to approximately room temperature before analysis.

3.3.3 The total sulfur method

To determine the reduction degree of a liquor, the sulfide content was first measured. Practically no sulfide ions are present due to the hydrolysis reaction $S^{2-} + H_2O \rightarrow HS^- + OH^-$, therefore it was the hydrogen sulfide content that was determined in practice.

1,0 ml of the sample was pipetted into a 150 ml beaker and placed on the automatic sample processor (Figure 1). 50 ml of the sodium hydroxide solution, 5 ml of ammonia and approximately 80 ml of water were added automatically and the mixture was titrated with the silver nitrate solution until the potentiometric EP (end point) was determined. The hydrogen sulfide content was calculated, in grams of sulfur per liter, though the formula

$$\text{Hydrogen sulfide content } \left(\frac{g}{L} \right) = \frac{c_{Ag^+} \times v_{Ag^+} \times 32,06}{v_s \times 1000 \times 2}$$

where c_{Ag^+} is the concentration of the silver nitrate solution (100 mM), v_{Ag^+} is the volume of the silver nitrate solution consumed in ml, 32,06 is the molar mass of sulfur (g/mol), v_s is the sample volume (1 ml), 1000 is the factor for the conversion of mmol to mol, and 2 accounts for the mole ratio in the reaction $HS^- (aq) + OH^- (aq) + 2Ag^+ (aq) \rightarrow Ag_2S (s) + H_2O$.

If a second end point was observed, this indicates the presence of polysulfide. The sample was then pretreated, and the analysis rerun. Approximately 10 ml of the alkaline sodium sulfite solution was heated to boiling. The beaker was taken off the heat and 1,0 ml of sample was added. The mixture was reheated to boiling and taken off after a few seconds and was allowed to cool. The mixture was reanalyzed through the same procedure as described above.

The total amount of sulfur was determined by first oxidizing all the sulfur compounds to sulfate. 2,0 ml of the sample was pipetted into a beaker and approximately 20 ml distilled water was added. Hydrogen peroxide was added slowly with a pipette, until the solution was clear and colorless, approximately 5 ml in total. An excess of hydrogen peroxide was ensured using a peroxide test strip, adding more if needed. The solution was heated and boiled until the reaction had finished. The sides of the beaker were rinsed with water throughout when a white coating was observed. The beaker was taken off the hot plate and 6-10 drops (depending on the amount of hydrogen peroxide added) of the cobalt(II) nitrate solution were added. The solution was heated for approximately a minute to destroy the excess hydrogen peroxide and was then allowed to cool. A lack of hydrogen peroxide was ensured using a peroxide test strip. If hydrogen peroxide remained, a few more drops of the cobalt(II) nitrate solution was added and the mixture was reheated. The solution was diluted to 100 ml and 20 ml of the diluted solution was pipetted into a 150 ml beaker and placed on the automatic sample processor. 80 ml of ethanol was added and the pH was adjusted to 4 with perchloric acid automatically. The solution was titrated with the lead(II) perchlorate solution until the potentiometric EP was determined. The occurring reaction has the formula $Pb^{2+} (aq) + SO_4^{2-} (aq) \rightarrow PbSO_4 (s)$. The total sulfur content was calculated using the formula

$$\text{Total sulfur content } \left(\frac{g}{L} \right) = \frac{32,06 \times v_{Pb^{2+}} \times c_{Pb^{2+}} \times f}{v_s \times 1000}$$

where 32,06 is the molar mass of sulfur (g/mol), v_{Pb2+} is the volume of the lead(II) perchlorate solution consumed in ml, c_{Pb2+} is the concentration of the lead perchlorate solution (50 mM), f is the dilution factor (50), v_s is the volume of the diluted oxidized sample solution (20 ml) and 1000 is the factor for the conversion of mmol to mol.

The reduction degree was calculated as a percentage of hydrogen sulfide out of total sulfur through

$$Reduction\ degree\ (\%) = \frac{Hydrogen\ sulfide\ content\ (\frac{g}{L})}{Total\ sulfur\ content\ (\frac{g}{L})} \times 100$$

When a new lead(II) perchlorate solution was prepared, its exact concentration was determined by performing the analysis on a sodium sulfate solution with a known concentration (50 mM). 5 ml of the sodium sulfate solution was pipetted in a 150 ml beaker and 15 ml of deionized water was added. 80 ml of ethanol was added and the pH was adjusted to 4 with perchloric acid automatically. The solution was titrated with the lead(II) perchlorate solution until the potentiometric EP was determined. The concentration was calculated using the formula

$$Concentration\ of\ lead(II)\ perchlorate\ (mM) = \frac{c_{SO4} \times 5}{v_{Pb2+}}$$

where c_{SO4} is the concentration of the sodium sulfate solution (50 mM), 5 is the volume of the sodium sulfate solution in ml and v_{Pb2+} is the volume of the lead(II) perchlorate solution consumed in ml. Three replicates were performed and the mean was calculated.

The method described is currently in use at Billerud Karlsborg and is based on the standard methods SCAN-N 31:94 and 5:83 [8,9].

To calculate a theoretical sulfate content from these results, an assumption had to be made that the only sulfur compounds in the sample were sulfide and sulfate. With this assumption, the sulfate content was calculated using the formula

$$Sulfate\ content\ (\frac{g}{L}) = \frac{totS - HS}{32,06} \times 96,06$$

where totS is the total sulfur content in g/L, HS is the sulfur content in the hydrogen sulfide measurement in g/L, 32,06 is the molar mass of sulfur in g/mol and 96,06 is the molar mass of sulfate in g/mol.

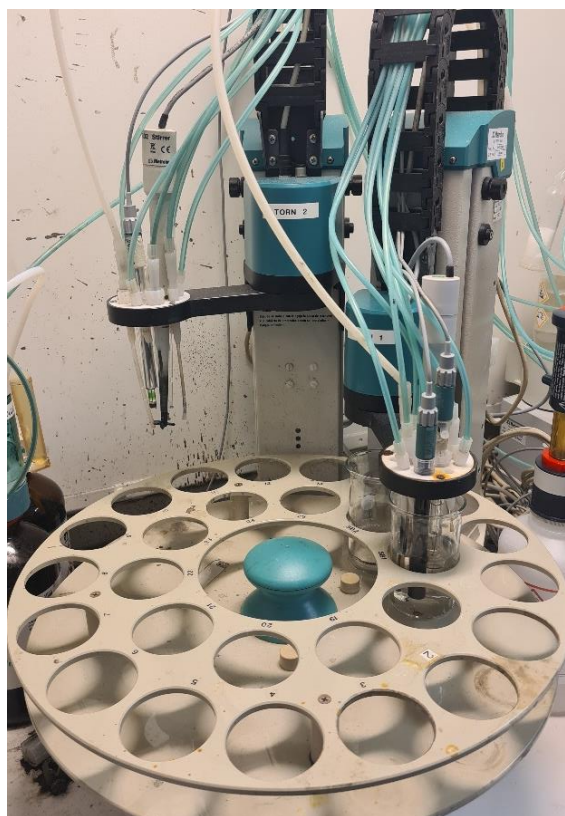


Figure 1: Automatic sample processor (Metrohm 814 USB Sample Processor) used in the total sulfur method and the formaldehyde method.

3.3.4 The formaldehyde method

In this method adjacent to the total sulfur titration, 16 ml of formaldehyde and 40 ml of acetone were added to a 150 ml beaker. 4 ml of the sample was added, avoiding any solid particles settled at the bottom. Samples were run one at a time and the program was started as soon as the sample had been added. The same automatic sample processor shown in Figure 1 was used in this method as well. 24 ml of water was automatically dispensed to dilute the formaldehyde and the pH was adjusted to $3,0 \pm 0,5$ with perchloric acid. The solution was titrated with the lead(II) perchlorate solution until the potentiometric EP was determined. The same reaction occurs as in the total sulfur titration. The sulfate content was calculated using the formula

$$\text{Sulfate content } \left(\frac{g}{L} \right) = \frac{96,06 \times v_{Pb2+} \times c_{Pb2+}}{1000 \times v_s}$$

where 96,06 is the molar mass of sulfate (g/mol), v_{Pb2+} is the volume of the lead(II) perchlorate solution consumed in ml, c_{Pb2+} is the concentration of the lead(II) perchlorate solution (50 mM), 1000 is the factor for the conversion of mmol to mol and v_s is the sample volume (4 ml).

The method is based on the standard method SCAN-N 6:85 [10], with all the volumes decreased by 20% to better fit the beakers used.

3.3.5 Thermometric titration

The reagent blank was determined for each new batch of sulfuric acid and acid mixture. About 10 ml of water was pipetted into the titration vessel and 20 ml of the acid mixture was automatically dispensed (see Figure 2). Thermometric titration with sulfuric acid was conducted three times. The mean of the volume of titrant consumed to reach the exothermic EP was calculated.

For the sample measurements, 10 ml of sample was pipetted into the titration vessel and 20 ml of the acid mixture, which contained an excess amount of barium ions, was automatically dispensed. The reaction was allowed to proceed and cool for 10 minutes. Thermometric titration with sulfuric acid was conducted in order to precipitate the remaining barium ions, and the volume of titrant consumed to reach the exothermic EP was noted. The occurring reaction has the formula $\text{Ba}^{2+} (\text{aq}) + \text{SO}_4^{2-} (\text{aq}) \rightarrow \text{BaSO}_4 (\text{s})$. The sulfate content was calculated using the formula

$$\text{Sulfate content } \left(\frac{\text{g}}{\text{L}} \right) = \frac{(CV_{\text{blank}} - V_{\text{EP}}) \times M \times c}{v_s}$$

where CV_{blank} is the mean volume (ml) titrant consumed in the reagent blank runs, V_{EP} is the volume (ml) titrant consumed until the EP, M is the molar mass of sulfate (96,06 g/mol), c is the concentration of the titrant (1 M) and v_s is the sample volume (10 ml).

The method described was provided by the instrument provider Metrohm.

To determine the reduction degree, the thermometric titration and the current sulfide titration would be performed, and it would be calculated using the formula

$$\text{Reduction degree } (\%) = \frac{\text{Sulfide content } \left(\frac{\text{g}}{\text{L}} \right)}{\text{Sulfide content } \left(\frac{\text{g}}{\text{L}} \right) + \text{Sulfate content } \left(\frac{\text{g}}{\text{L}} \right)}$$

where the sulfate content in grams of sulfate per liter have been recalculated to grams of sulfur per liter by dividing by 96,06 and multiplying by 32,06.



Figure 2: Equipment used in the thermometric titration (Metrohm 859 Titrotherm)

3.3.6 Alkali R

Alkali R (see Figure 3) measures the sulfide content through an ABC titration based on the standard method SCAN 30:85, which is a potentiometric titration with 1 M hydrochloric acid. The pH was monitored and 3 EPs were determined. Alkali R expresses all results as grams of NaOH per liter for easier comparison and further calculations in the process. The sodium sulfide content was calculated using the formula

$$\text{Sodium sulfide content } \left(\frac{g}{L} \right) = \frac{(2A - 4B + 2C) \times N \times M}{V}$$

where A is the consumption (in ml) of hydrochloric acid at the first EP, B at the second, and C at the third, N is the normality of the hydrochloric acid (1 N), M is the molar mass of sodium hydroxide (40 g/mol) and V is the sample volume (2 ml).

To convert the results to grams of sulfur per liter, the analyzer value must be divided by 2 (to account for the molar ratio of sodium in NaOH and Na₂S) and then 40 (the molar mass of sodium hydroxide) and multiplied by 32,06 (the molar mass of sulfur).

The sulfate content was measured by mixing 1 ml of the sample with 45 ml isopropanol and titrating with 0,025 M barium chloride until an optical inflection point was detected. The sulfate content was calculated using the formula

$$\text{Sodium sulfate content } \left(\frac{g}{L} \right) = \frac{2 \times D \times N \times M}{V}$$

where D is the consumption (in ml) of barium chloride at the EP, N is the concentration of barium chloride (0,025 M), M is the molar mass of NaOH (40 g/mol) and V is the sample volume (1 ml).

To convert the results to grams of sulfate per liter, the analyzer value must be divided by 2 (to account for the molar ratio of sodium in NaOH and Na₂SO₄) and then 40 (the molar mass of sodium hydroxide) and multiplied by 96,06 (the molar mass of sulfate).

When the reduction degree is calculated, the total amount of sulfur is assumed to be the sulfide content plus the sulfate content.

Samples of white and green liquor were taken for 10 days directly from the analyzer to get as comparable samples as possible. The liquors were analyzed according to the above-described methods and all data points were added to the method comparison statistical analysis. The green liquor results were also compared with the Alkali R results.

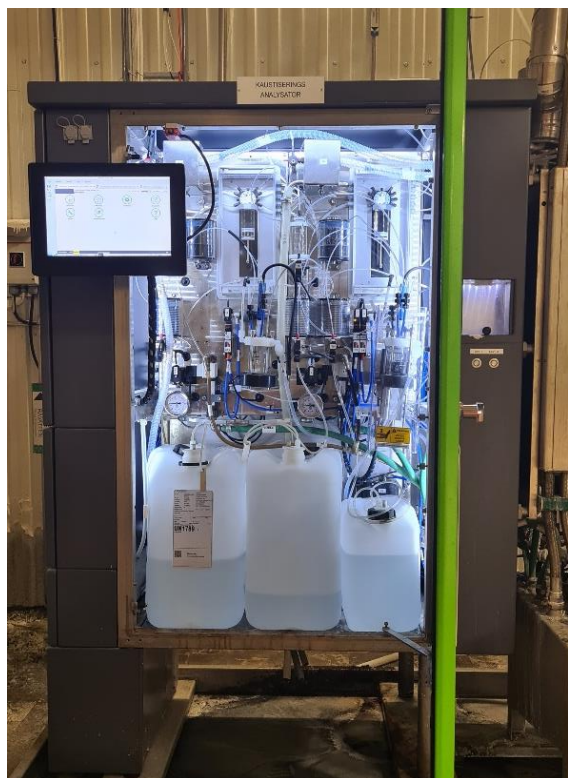


Figure 3: Alkali R recovery liquor analyzer. Samples were collected through the small hatch door on the right-hand side.

4 Results and discussions

4.1 Method validation

4.1.1 The formaldehyde method

From the 11 replicate measurements with a 0,10 g/L sulfate standard solution, the standard deviation was calculated to be 0,02 g/L, the LOD (defined as 3 times the standard deviation) to be 0,06 g/L and the LOQ (defined as 10 times the standard deviation) to be 0,20 g/L. The raw data can be found in RD 1 (Raw data 1 in the appendix).

The results for the linear range measurements are shown in Figure 4. The measured value dots show the average for the 5 replicates. The linear range was determined by visual inspection to approximately be from the LOQ all the way up through the tested range (to 15 g/L). The coefficient of determination (R^2) for the linear regression is extremely good, as it rounds up to exactly 1 when 4 decimal precision is used. The raw data can be found in RD 2.

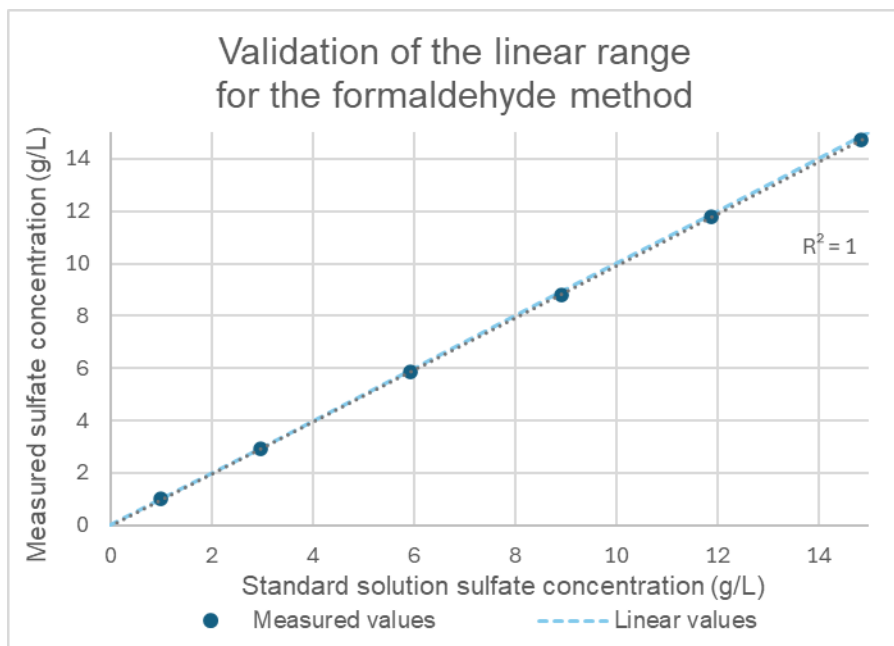


Figure 4: Validation of the linear range of the formaldehyde method. Dark blue dots show the mean of the 5 replicate measurements at each concentration. The variance between the replicates is so small that the added error bars are not visible. Light blue dotted line shows where the values would fall if the method was accurate at that concentration range. Grey dotted line shows the linear regression of the measured value points.

The results for the trueness and precision measurements for the 2 g/L stock solution were: mean 1,996 g/L, standard deviation 0,005 g/L, relative standard deviation 0,25%, bias 0,004 g/L

and relative bias 0,18%. For the 5 g/L stock solution they were: mean 4,977 g/L, standard deviation 0,009 g/L, relative standard deviation 0,18%, bias 0,023 g/L and relative bias 0,45 %. The raw data can be found in RD 3.

4.1.2 Thermometric titration

The three reagent blank measurements gave the results 3,25; 3,25 and 3,24 ml of titrant consumed to reach the EP, so the reagent blank was set as 3,25 ml.

From the 11 blank measurements (deionized water), which still gave EPs and resulting calculated sulfate contents, the standard deviation was calculated to be 0,06 g/L, LOD (3 times the standard deviation) to be 0,17 g/L and LOQ (10 times the standard deviation) to be 0,56 g/L. The raw data can be found in RD 4.

The results for the linear range measurements are shown in Figure 5. The measured value dots show the average for the 5 replicates. The linear range was determined by visual inspection to approximately be from the LOQ to 6 g/L (this point was chosen by where the measured mean deviates from the standard approximately 10%, here 10,9%). The raw data can be found in RD 5.

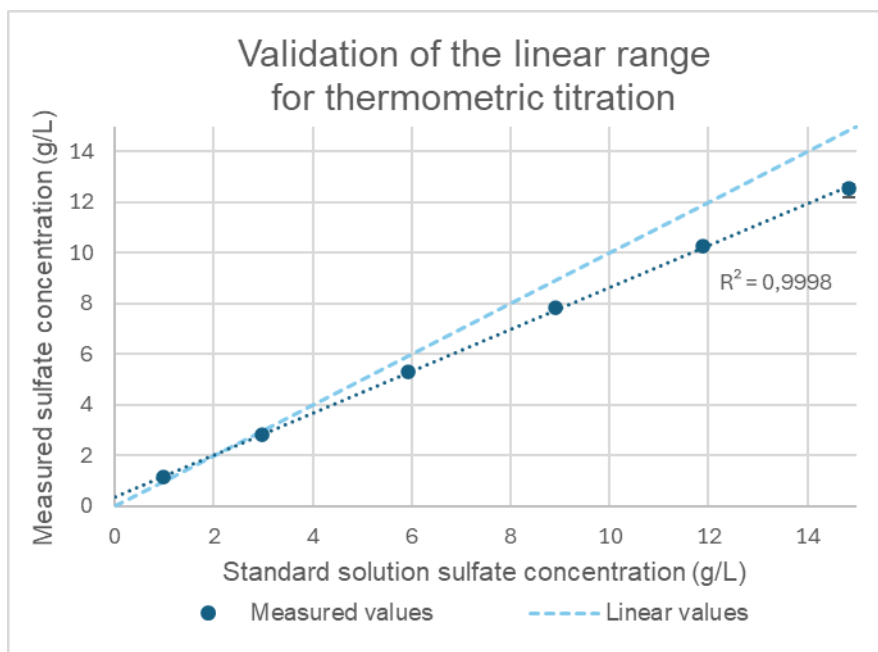


Figure 5: Validation of the linear range of the thermometric titration method. Dark blue dots show the mean of the 5 replicate measurements at each concentration. The variance between the replicates is so small that the error bars are barely visible. Light blue dotted line shows where the values would fall if the method was accurate at that concentration range. Grey dotted line shows the linear regression of the measured value points.

Interestingly enough though, the measurement points fall on a very straight line, yielding a R^2 value of 0,9998, but they simply aren't accurate at higher concentrations. We can therefore see that the deviation from the standard concentrations seem to increase linearly from 6 g/L and up. This appears to hold true when the percentage deviation is plotted against the standard concentrations (see Figure 6), yielding an R^2 value of 0,9927. This could potentially be useful in calculating more accurate results if values above the linear range are obtained.

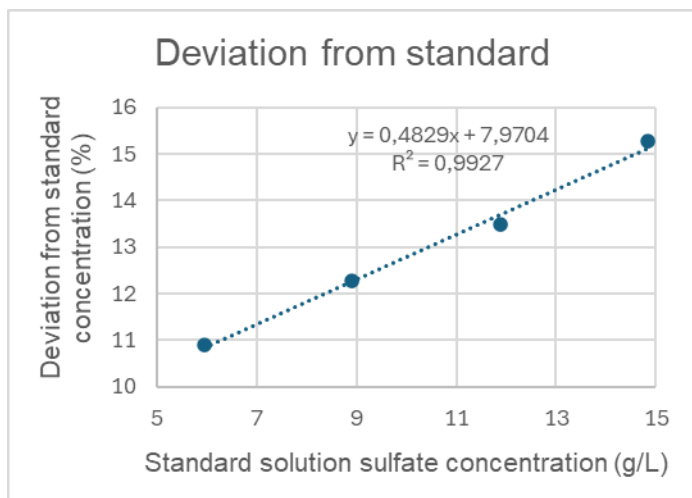


Figure 6: Percentage deviation from the standard concentration in the thermometric titration validation results.

The results for the trueness and precision measurements for the 2 g/L stock solution were: mean 1,960 g/L, standard deviation 0,044 g/L, relative standard deviation 2,27%, bias 0,044 g/L and relative bias 2%. For the 5 g/L stock solution they were: mean 4,555 g/L, standard deviation 0,042 g/L, relative standard deviation 0,93%, bias 0,445 g/L and relative bias 8,9%. The raw data can be found in RD 6.

4.1.3 Validation result comparison

Table 1: Summary of the validation results for the formaldehyde method and the thermometric titration.

	Formaldehyde method	Thermometric titration
LOD	0,06 g/L	0,17 g/L
LOQ	0,20 g/L	0,56 g/L

Linear range	0,20 – 15 g/L	0,56 – 6 g/L
Trueness & precision at 2 g/L		
Mean	1,996 g/L	1,960 g/L
Standard deviation	0,005 g/L	0,044 g/L
Relative standard deviation	0,25%	2,27%
Bias	0,004 g/L	0,044 g/L
Relative bias	0,18%	2%
Trueness & precision at 5 g/L		
Mean	4,977 g/L	4,555 g/L
Standard deviation	0,009 g/L	0,042 g/L
Relative standard deviation	0,18 %	0,93%
Bias	0,023 g/L	0,445 g/L
Relative bias	0,45%	8,9%

When comparing the validation results for both methods, summarized in Table 1, we can see that the formaldehyde method is significantly better in most points. When it comes to the LOD and LOQ, it is necessary to see where the actual sample values tend to fall, because if they are well above these values for both methods, then this shouldn't be a determining factor in if the thermometric titration is an adequate replacement for the current method.

The formaldehyde method was linear and accurate in the entire tested range, and the thermometric titration only up to approximately 6 g/L. However, as with LOD and LOQ, the importance of this factor also depends on where the actual sample values fall.

In the trueness and precision measurements, the thermometric titration performed better at 2 g/L than 5 g/L, which was to be expected from the linearity plot. At 5 g/L the standard deviation was almost the same as at 2 g/L, indicating a similar precision at both concentrations, but the relative bias was 8,9%, in comparison with 2% at 2 g/L. The method is therefore less accurate at 5 g/L, which, again, was expected from the linearity plot, but the deviation is still under 10% which should be an acceptable deviation in this case. The formaldehyde method was more precise and truer than the thermometric titration at both concentrations. It also performed better at 2 g/L than 5 g/L, but only slightly, all the relative standard deviations and biases were well under 1%.

It is necessary to remember, however, that the formaldehyde method might not be a fully accurate representation of the current method, since the sample pretreatments differ in multiple ways, and therefore many other factors must be considered in the method comparison itself.

Another point to consider is that there could also be differences in how the methods perform with actual samples in comparison with the standard solutions.

4.2 Method comparison

There are two main ways to compare the thermometric titration to the current method: Comparing the sulfate content results from the thermometric titration with the formaldehyde method, and comparing reduction degrees calculated through the current method and the proposed one.

Samples 1-10 were collected from the regular sample collection points (23-27/9/2024 and 30/9-4/10/2024), and 11-20 directly from the Alkali R recovery liquor analyzer (8-11/10/2024, 14-16/10/2024, 18/10/2024 and 21-22/10/2024).

4.2.1 Sulfate content: The formaldehyde method and the thermometric titration

Figures 7-10 summarize all the direct measurement results for the general method comparison. Figures 7 and 9 show the total sulfur and sulfide results with the current method for white and green liquor, respectively. Figures 8 and 10 show all the sulfate results from the formaldehyde method, the thermometric titration and the calculated sulfate content from the total sulfur method (Tot S*) by assuming that all sulfur in the liquor is either sulfide or sulfate. All the sulfate results are in grams of sulfate per liter (as opposed to grams of sulfur per liter for total sulfur and hydrogen sulfide results). The raw data can be found in RD 7 and 8.

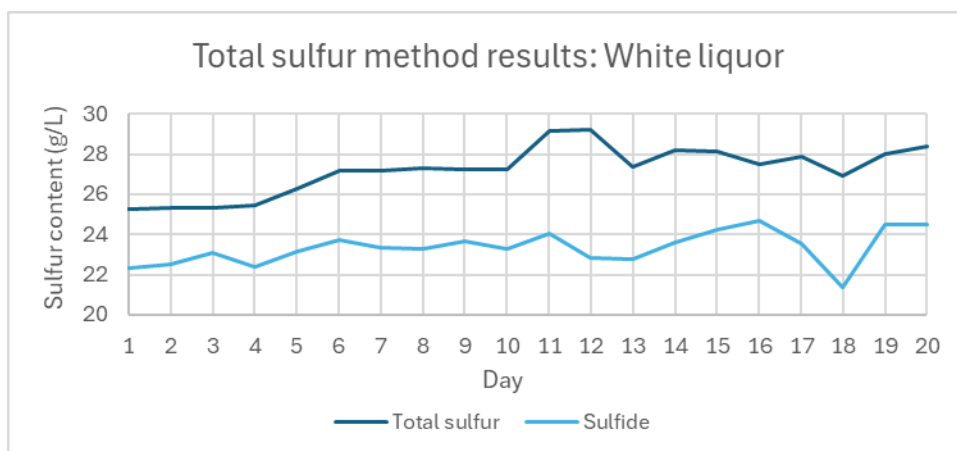


Figure 7: Results from the current total sulfur method for white liquor.

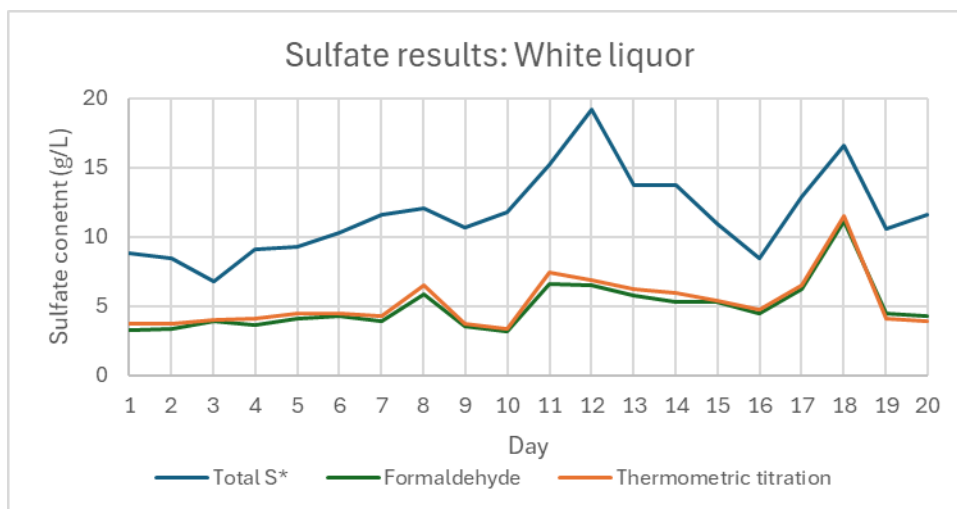


Figure 8: All sulfate results for white liquor.

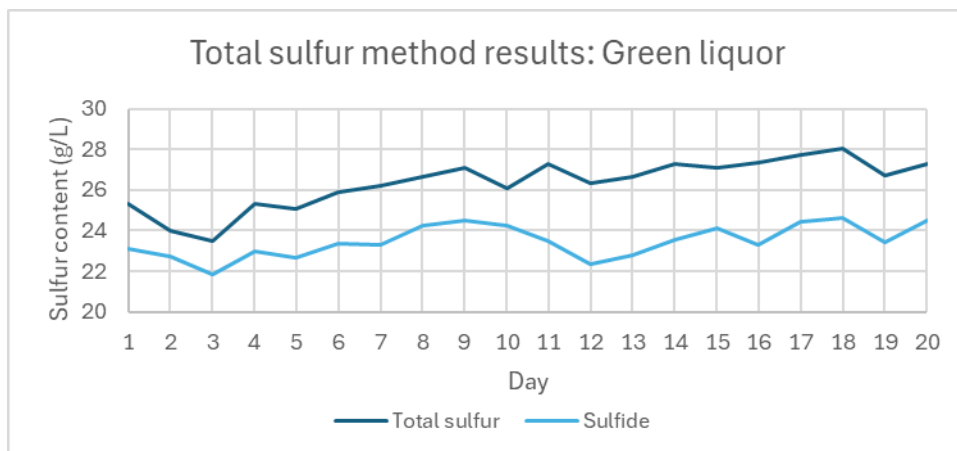


Figure 9: Results from the current total sulfur method for green liquor.

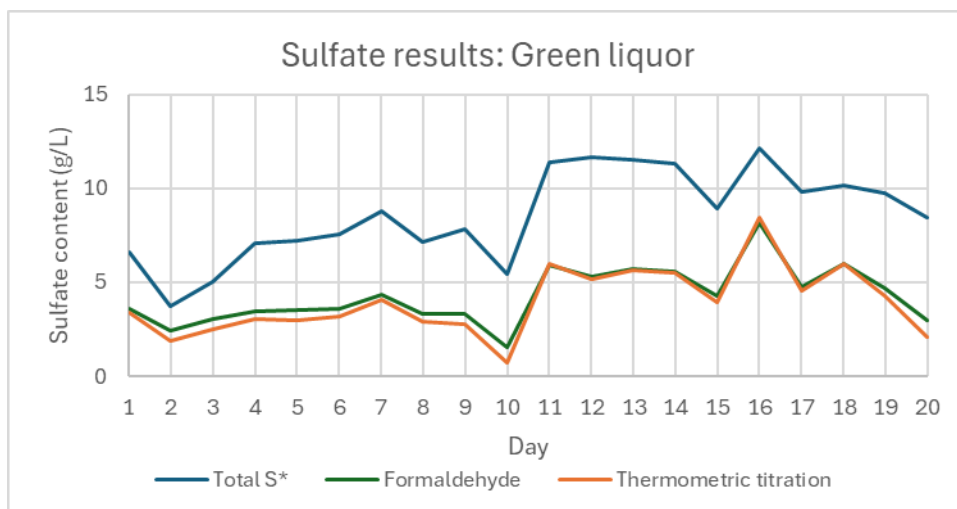


Figure 10: All sulfate results for green liquor.

Firstly, the formaldehyde method and thermometric titration results were compared by a Bland-Altman plot and with a paired t-test to see how statistically equivalent the methods are. For all the Bland-Altman plots in this section, the critical t-value for 19 freedom degrees, 2,093, was used in the calculation of the LOAs. Histograms showing approximate normal distribution for the differences were plotted for all statistical comparisons and they can be found in the appendix.

The Bland-Altman plot for the white liquor results in Figure 11 doesn't show a correlation between the average concentration and the method differences. We can simply see that in all except 2 samples the result from the thermometric titration was higher than for the formaldehyde method. These samples are also the only ones that fall outside the limits of agreement (dotted lines), which show the 95% confidence limits. The mean and standard deviation for the method differences, as well as the calculated t-value for the paired t-test, can be found in Table 2.

Table 2: Statistical values for the sulfate result differences for the formaldehyde method and the thermometric titration for the white liquor samples.

Mean (g/L)	Standard deviation (g/L)	t-value
0,304	0,285	4,77

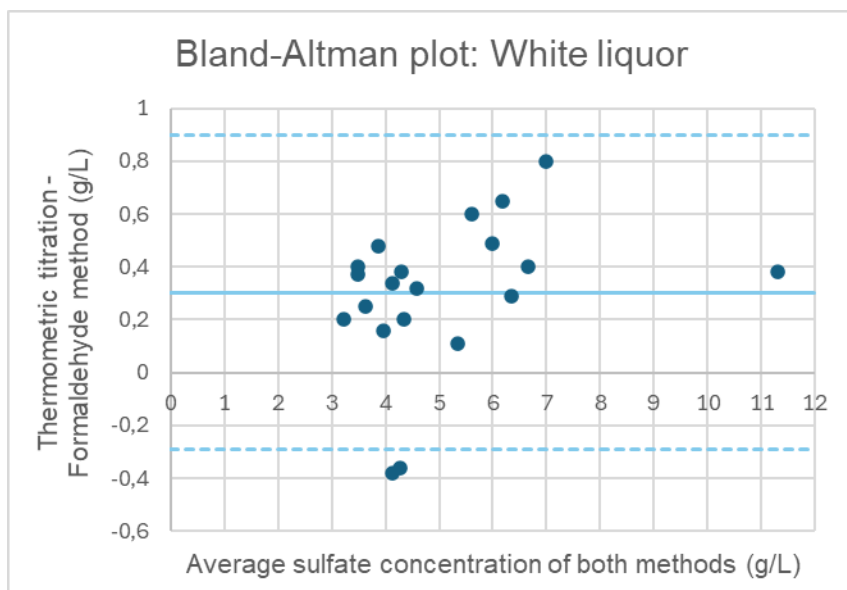


Figure 11: Bland-Altman plot for the white liquor results using the formaldehyde method and the thermometric titration. The middle horizontal line shows the mean deviation and the dotted lines show the upper and lower LOAs. The distribution is shown in Histogram 1 in the appendix.

In the green liquor results in Figure 12, however, an approximate linear correlation can be seen in the Bland-Altman plot. The lower the average concentration, the larger the deviation, the formaldehyde method having higher values instead. The methods get more equal the closer the average gets to approximately 6 g/L. 1-2 measurement points indicate that the thermometric titration values are higher after this point. For the green liquor measurements only one point falls outside 95% confidence interval. The mean and standard deviation for the method differences, as well as the calculated t-value for the paired t-test, can be found in Table 3.

Table 3: Statistical values for the sulfate result differences for the formaldehyde method and the thermometric titration for the green liquor samples.

Mean (g/L)	Standard deviation (g/L)	t-value
-0,323	0,284	5,08

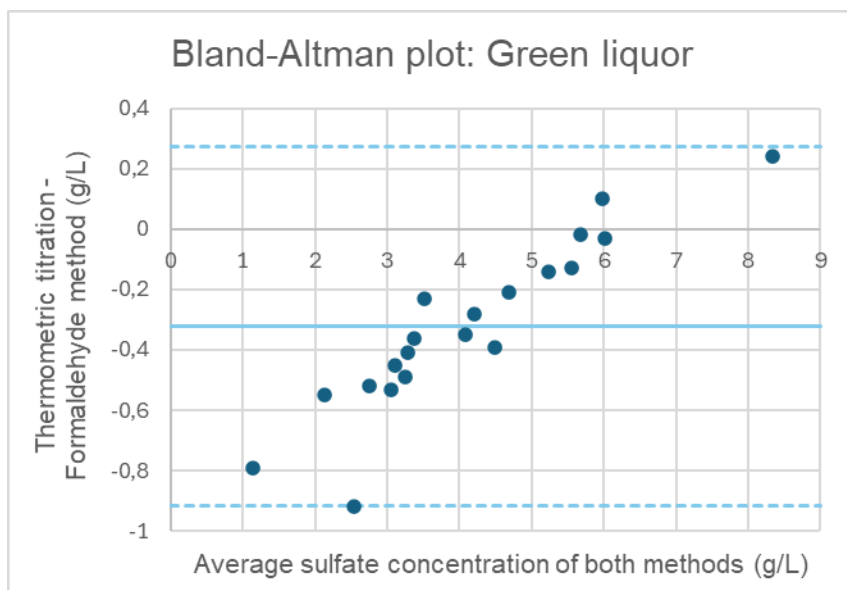


Figure 12: Bland-Altman plot for the white liquor results using the formaldehyde method and the thermometric titration. The middle horizontal line shows the mean deviation and the dotted lines show the upper and lower LOAs. The distribution is shown in Histogram 2 in the appendix.

In the validation experiments, when the analyses were performed with standard solutions, the formaldehyde method was very accurate. This is why the comparison between these two methods, with the formaldehyde method as the reference point, was used as a test on the performance of the thermometric titration. Above approximately 2 g/L, the thermometric titration was more and more below the actual standard concentration with increasing concentration. If the experiments with liquor samples were to follow this same pattern, the formaldehyde method results should have been higher above 2 g/L. This was, however, not the case, where the results are actually flipped for the two different liquors. When calculating thermometric titration minus the formaldehyde method, the difference was mostly positive for white liquor and mostly negative for green liquor. A possible explanation for this is that some unexpected reactions were observed in the acetone-formaldehyde-sample mixture before the titration had even been started, where the color turned bright orange and a dark precipitate was formed if left too long. This is why the samples were analyzed one at a time and the titration run was started as fast as possible. This reaction seemed to be faster and stronger for the white liquor mixtures, possibly due to the much higher hydroxide content catalyzing this unknown reaction. If, despite the immediate start, some of this reaction had started to happen, and if this precipitate contained sulfate, this could explain the lower results for the white liquor samples with the formaldehyde method. Since the methods performed different than expected, we can't assume that the formaldehyde method results are more accurate. Since the formaldehyde method isn't a reliable reference point, a larger deviation from it might not necessarily imply a fault in the thermometric titration. The t-values from the paired t-test were 4,77 and 5,08 for white and green liquor, respectively, which implies that these methods are not statistically equivalent since both values

exceed the critical value 2,093 for 19 freedom degrees (n-1) and a 95% confidence level. But again, equivalence or lack thereof to an unreliable reference method doesn't result in reliable conclusions.

Another observation that is worth noting, although it is not believed to have had significant impact, is that during the thermometric titration, significant bubbling was observed upon addition of the acid mixture to the sample, which could have resulted in barium ions being left on the sides of the vessel that then wouldn't react in the titration. The shapes of the titration curves for the two liquors were also different, where the green liquor curve first had a positive slope and then a negative, and this peak was the EP. For the white liquor the slope was negative the whole time, likely due to the mixture still being warmer despite the waiting time, but the EP was still clearly found where the slope went from negative to even more negative.

In Figures 8 and 10, the theoretical calculated sulfate content from the total sulfur method is also shown. These values are much higher than either of the two methods discussed. When calculating the differences total sulfur method minus formaldehyde method, the means are (for white and green liquor) 6,63 g/L and 4,30 g/L and the standard deviations are 2,09 g/L and 1,26 g/L. This implies the existence of other sulfur compounds that are mistakenly assumed to be sulfate. This will be discussed further later in the report.

4.2.2 Reduction degree: The total sulfur method and the thermometric titration

The raw data used for the figures in this section can be found in RD 9 and 10. The thermometric titration reduction degree was calculated by assuming that the total amount of sulfur is sulfate plus sulfide.

Figures 13 and 14 show the Bland-Altman plots for these results. Neither show any clear correlation between the average reduction degree and the method differences, but higher reduction degrees may potentially imply a smaller deviation. We can see that the bias (difference mean) is slightly lower for green liquor, and the standard deviation is also smaller so the methods are more similar for green liquor analysis. The means and standard deviations for the method differences, as well as the calculated t-values for the paired t-tests, can be found in Tables 4 and 5.

Table 4: Statistical values for the reduction degree differences for the total sulfur method and the thermometric titration for the white liquor samples.

Mean (Percentage points)	Standard deviation (Percentage points)	t-value
7,16	2,07	15,4

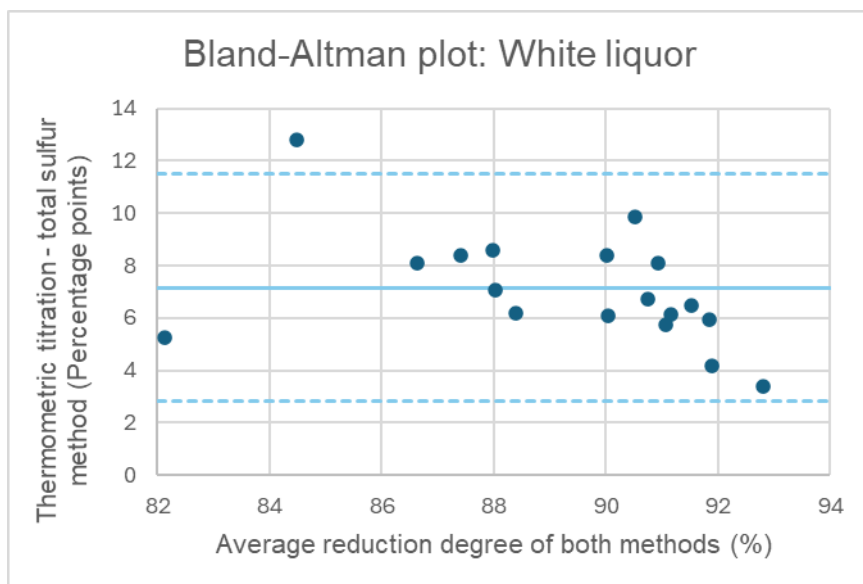


Figure 13: Bland-Altman plot for the white liquor results using the total sulfur method and the thermometric titration. The middle horizontal line shows the mean deviation and the dotted lines show the upper and lower LOAs. The distribution is shown in Histogram 3 in the appendix.

Table 5: Statistical values for the reduction degree differences for the total sulfur method and the thermometric titration for the green liquor samples.

Mean (Percentage points)	Standard deviation (Percentage points)	t-value
5,54	1,35	18,4

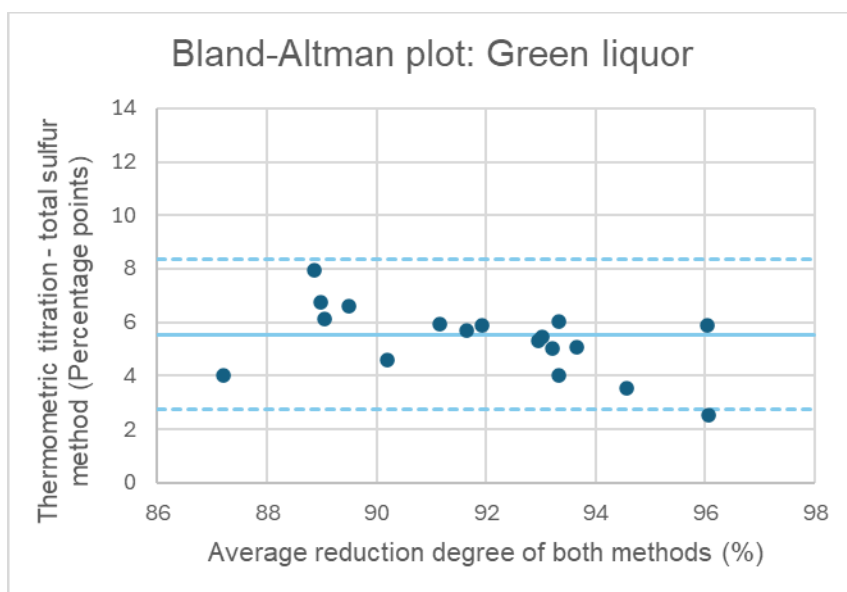


Figure 14: Bland-Altman plot for the green liquor results using the total sulfur method and the thermometric titration. The middle horizontal line shows the mean deviation and the dotted lines show the upper and lower LOAs. The distribution is shown in Histogram 4 in the appendix.

The total sulfur method and the thermometric titration are clearly not statistically equivalent, both t-values being above 15 (see Tables 4 and 5), which is well above 2,093. But the differences likely lie in the different definitions used to calculate the reduction degree, where the total sulfur method inherently includes other possible sulfur compounds, which the thermometric titration method does not. Since the same sulfide content is used in both calculations, the total amount of sulfur is what determines the difference in reduction degree, which again is influenced by the assumption of whether or not other sulfur compounds are present in the liquor. If we trust the accuracy of the thermometric titration, it would imply a significant amount of these non-sulfide and non-sulfate compounds. But this possibility is better confirmed or denied by a comparison with the more established method, Alkali R.

But before we get to that, we can also look at the change in reduction degree over time for both methods and both liquors. Figures 15 and 16 show line graphs presenting exactly this, where we can see that both methods tend to follow a similar trend, especially for green liquor. This would show that the concentration of the possible other sulfur compounds is somewhat consistent. If this consistency could be proven with reasonably small variations, this knowledge could be utilized to convert between both definitions of reduction degree. If the thermometric titration was implemented as the main method, a theoretical total sulfur reduction degree could also be calculated. Another way to go about it could be, that if an acceptable baseline reduction degree result was established for the thermometric titration, one could simply track the deviations from it and adjust the process based on them, and therefore what the actual value of the baseline was wouldn't matter as much.

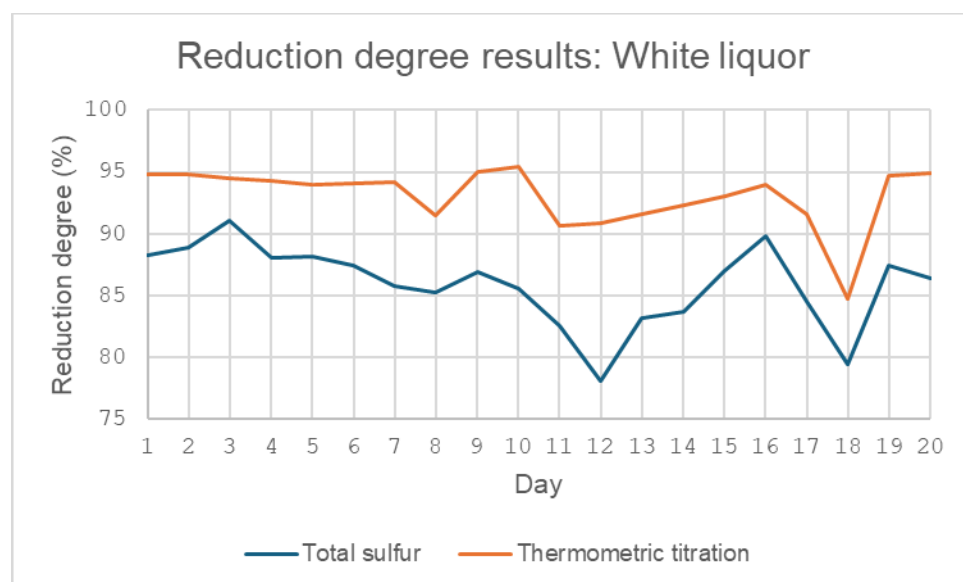


Figure 15: Line graph of the change in reduction degree for white liquor.

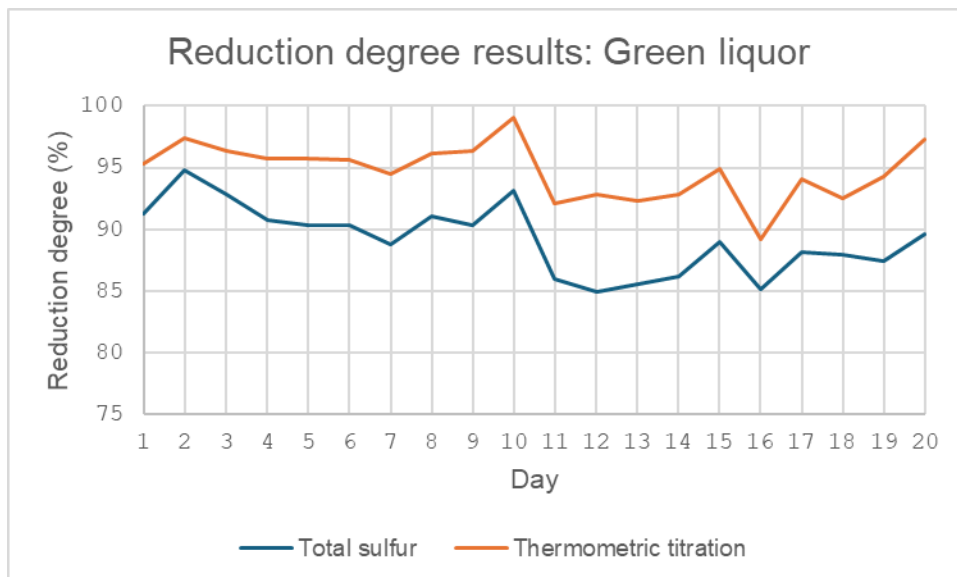


Figure 16: Line graph of the change in reduction degree for green liquor.

4.3 Alkali R comparison

When comparing the green liquor analysis results with the Alkali R recovery liquor analyzer, we can also compare both the sulfate content and reduction degree results. These samples were collected 8-11/10/2024, 14-16/10/2024, 18/10/2024 and 21-22/10/2024 directly from the analyzer.

4.3.1 Sulfate content: Alkali R, the formaldehyde method and the thermometric titration

Figure 17 summarizes the sulfate results for the formaldehyde method, thermometric titration and Alkali R. The raw data can be found in RD 12.

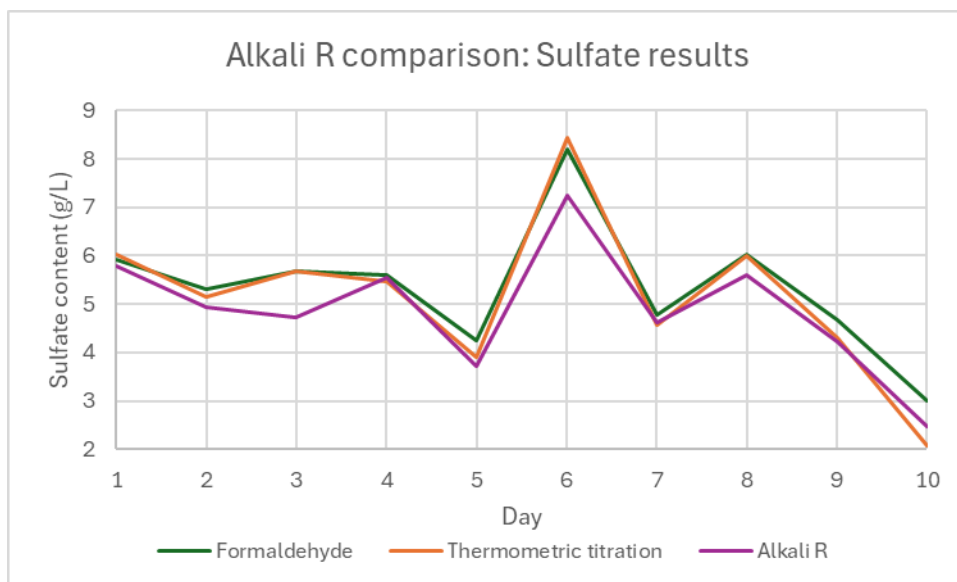


Figure 17: Sulfate results for the formaldehyde method, the thermometric titration and Alkali R.

Figures 18 and 19 show the Bland-Altman plots for the formaldehyde method and thermometric titration individually compared to the Alkali R results. The critical t-value for 9 freedom degrees, 2,262, was used in the calculation of the LOAs. The standard deviation of the differences is a bit smaller for the formaldehyde method (see Table 6), but the difference mean is closer to zero for the thermometric titration (see Table 7). The thermometric titration actually falls under the critical t-value, which would imply that the Alkali R method and the thermometric titration are statistically equivalent. It is important to note, however, that the differences for both methods aren't as close to normally distributed as in the earlier histograms, which makes the calculated t-value less reliable. We should still be able to assume that the thermometric titration is more equivalent to Alkali R than the formaldehyde method is. This further contributes to the discussion in section 4.2 leading to the conclusion that the formaldehyde method should not be used as the reference point in deciding if the thermometric titration is an adequate alternative method.

Table 6: Statistical values for the sulfate result differences between the formaldehyde method and Alkali R for the green liquor samples.

Mean (g/L)	Standard deviation (g/L)	t-value
0,460	0,309	4,70

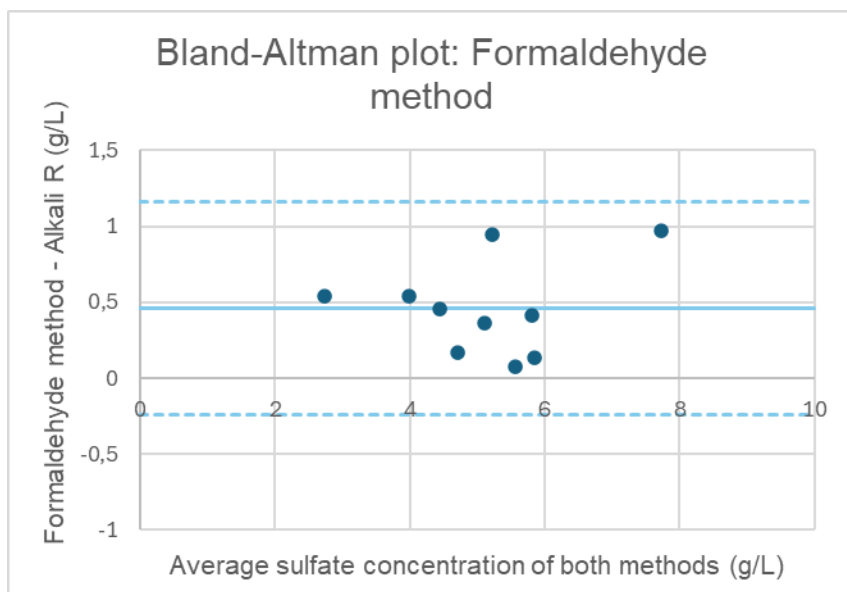


Figure 18: Bland-Altman plot for the green liquor results using the formaldehyde method and Alkali R. The middle horizontal line shows the mean deviation and the dotted lines show the upper and lower LOAs. The distribution is shown in Histogram 5 in the appendix.

Table 7: Statistical values for the sulfate result differences between the thermometric titration and Alkali R for the green liquor samples.

Mean (g/L)	Standard deviation (g/L)	t-value
0,275	0,472	1,84

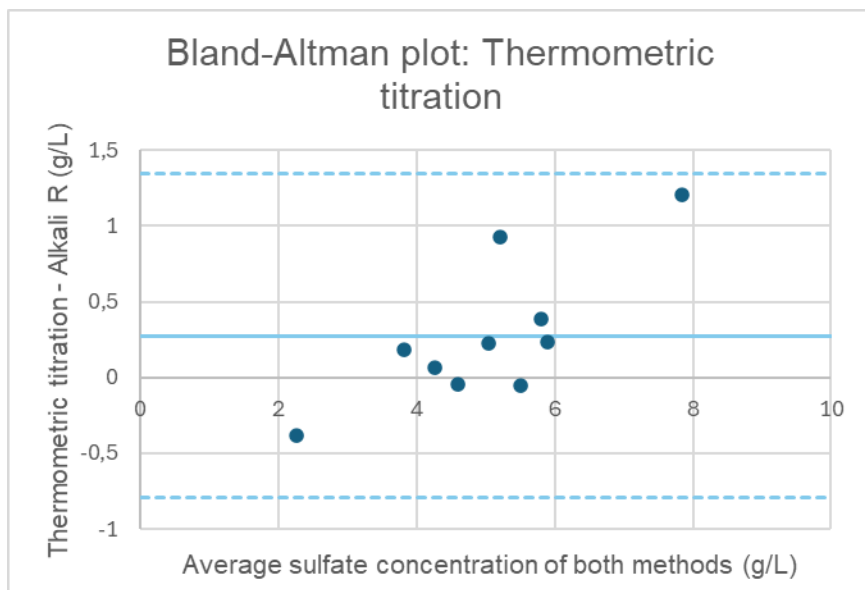


Figure 19: Bland-Altman plot for the green liquor results using the thermometric titration and Alkali R. The middle horizontal line shows the mean deviation and the dotted lines show the upper and lower LOAs. The distribution is shown in Histogram 6 in the appendix.

4.3.2 Reduction degree: Alkali R, the total sulfur method and the thermometric titration

The calculated reduction degrees with Alkali R, the total sulfur method and the thermometric titration, which were used for the figures in this section, can be found in RD 13.

Figure 20 shows a Bland-Altman plot where the x-axis is the Alkali R reduction degree results and the y-axis is the deviation from them, showing the total sulfur method in blue and the thermometric titration in orange. From this plot we can clearly see that the thermometric titration is both more accurate and precise than the total sulfur method if the Alkali R results are used as the reference point. The t-value (see Table 8) for the thermometric titration is also below the critical value 2,26, indicating that the two methods are statistically equivalent. The differences shown in Histogram 8 are also sufficiently normally distributed, making the t-value reliable. Some values being negative and some positive is also a good sign that indicates that there isn't any systematical error shifting the values one way or the other.

Table 8: Statistical values for the differences in reduction degree results between Alkali R and the total sulfur method, as well as between Alkali R and the thermometric titration.

	Mean (Percentage points)	Standard deviation (Percentage points)	t-value
Total sulfur method	6,34	1,15	17,4
Thermometric titration	0,515	0,588	0,810

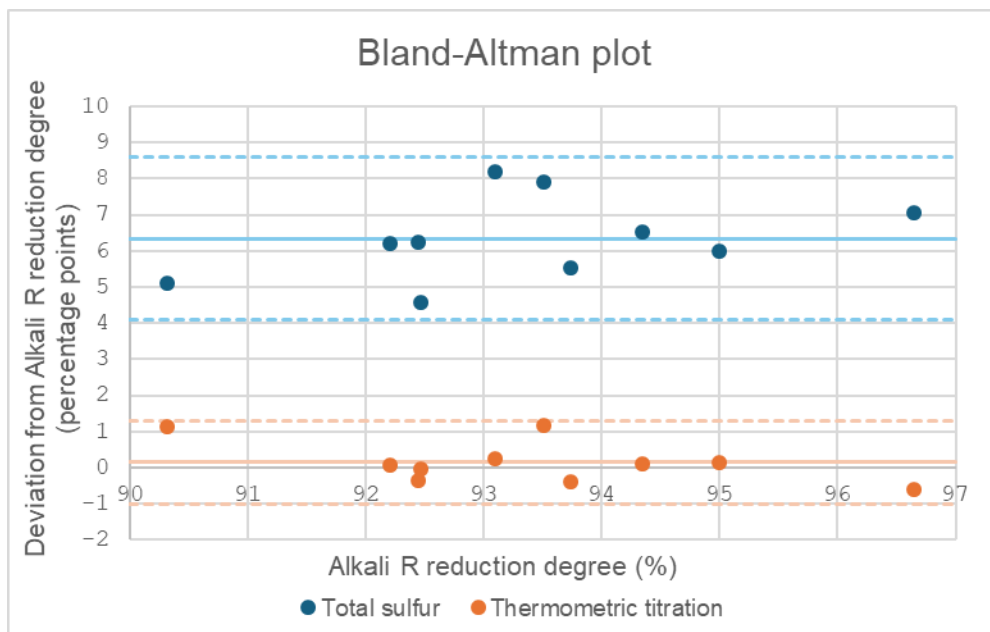


Figure 20: Bland-Altman plot for the green liquor results using the total sulfur method, thermometric titration and Alkali R. The middle horizontal line shows the mean deviation and the dotted lines show the upper and lower LOAs. The distributions are shown in Histograms 7 and 8 in the appendix.

In Figure 21 a line graph shows the reduction degree over time for all three methods. Here we can again see that the thermometric titration and Alkali R follow almost the same line, and the total sulfur method falls below, with an almost consistent deviation. This further strengthens the point that there likely are some other sulfur compounds, since now two methods indicate the same thing.

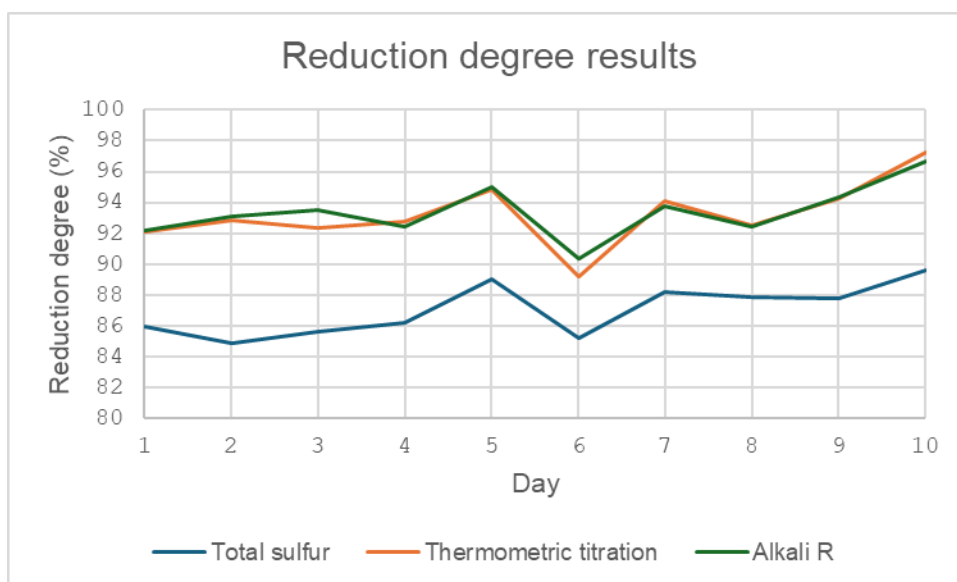


Figure 21: Line graph of the change in reduction degree for green liquor, comparing the total sulfur method, thermometric titration and Alkali R.

4.3.3 Total sulfur content: Alkali R and the total sulfur method

Figure 22 summarizes the total sulfur results for Alkali R and the total sulfur method. The raw data can be found in RD 14.

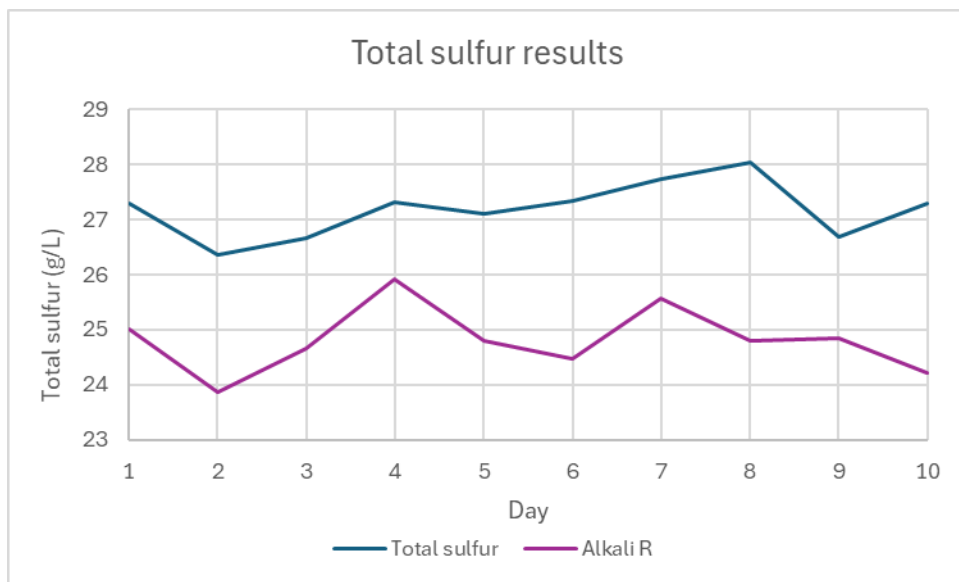


Figure 22: Total sulfur results for Alkali R and the total sulfur method.

Figure 23 shows the difference on the y-axis and the sulfur content from the total sulfur method on the x-axis. Since there is no clear correlation between the points, the amount of suspected other sulfur compounds isn't a set fraction of the total sulfur amount, but instead has some day-to-day variation. These values range from 1,39 to 3,22 and have a mean of 2,37. This, with the earlier points, would strongly indicate that the reason for the differences between the current laboratory method and Alkali R is due to the occurrence of other sulfur compounds that are not accounted for in the calculation of total sulfur in Alkali R.

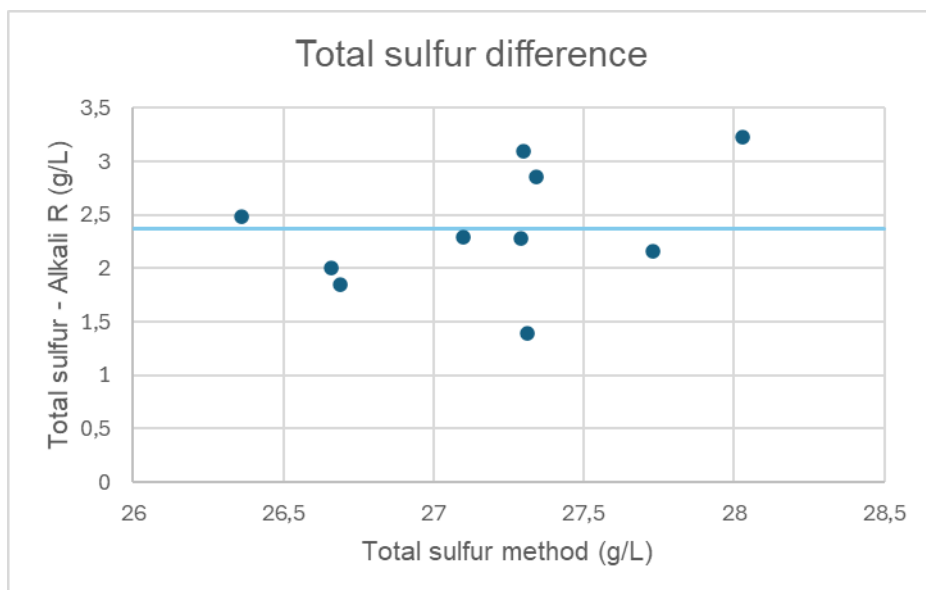


Figure 23: The difference in the total amount of sulfur between the total sulfur method and Alkali R.

5 Conclusions

Due to the formaldehyde method yielding inconsistent results with liquor samples in comparison to the standard solution validation, this method will not be used as a reference point to determine the adequacy of the thermometric titration.

When the thermometric titration reduction degree was compared with the current total sulfur method, these methods were not statistically equivalent, but this is most likely because of the different definitions used in the calculation of the reduction degrees. The comparisons with Alkali R, however, both when comparing sulfate content and reduction degree, strongly show that the thermometric titration results are equivalent to the Alkali R results, and therefore, if this is the most important criteria for replacing the current method, the thermometric titration is fully adequate.

When it comes to the second aim, all performed comparisons indicate that the discrepancies between the total sulfur method and Alkali R are due to the existence of other sulfur compounds in the liquors.

6 Future aspects

If Billerud Karlsborg concludes that the thermometric titration is an adequate replacement based on these results and wants to proceed onto more detailed validation experiments, some improvements or changes can be made to see how these affect the results.

As mentioned in section 4.2, it was observed that the white liquor samples may not have been sufficiently cooled off before the titration. It is therefore advisable to try performing the experiment with a longer waiting time than 10 minutes to ensure that this does not have a significant impact on the results. Another possible attempt to get even more precise results would be to dilute the liquor samples so that their concentration would be closer to 2 g/L which was the most accurate point according to the validation. The sulfate results tended to be mostly around 3-6 g/L, so a 2 times dilution would be suggested.

The amount and significance of the other sulfur compounds in the process should also be studied. Further datapoints over a longer time period would give knowledge on if the content or fraction of the compounds is consistent. If it turns out to not be consistent, a suggestion would be to still perform the lead perchlorate titration, but less often, to be aware of general major changes, but still reduce the use of this chemical.

7 References

- [1] Skogsindustrierna. (2024, August 28). *Snabba fakta - Den svenska skogsindustrin i korthet*. Retrieved October 17, 2024, from <https://www.skogsindustrierna.se/om-skogsindustrin/branschstatistik/snabba-fakta/>
- [2] Biermann, C. J. (1996). *Handbook of pulping and papermaking*. (2. Ed.). (pp. 13-14, 36, 86). Academic press.
- [3] Bajpai, P. (2017). *Pulp and Paper Industry: Chemical Recovery*. (pp. 5, 6, 39, 67-68, 82, 101-104, 119). Elsevier.
- [4] Grace, T. M. (1992). Chemical Recovery Process Chemistry. In R. P. Green & G. Hough (Eds.), *Chemical Recovery in Alkaline Pulping Processes* (p. 57). Technical Association of the Pulp & Paper Industry (TAPPI).
- [5] Cornell, C. F. (1992) Cooking Liquor Preparation. In R. P. Green & G. Hough (Eds.), *Chemical Recovery in Alkaline Pulping Processes* (p. 124). Technical Association of the Pulp & Paper Industry (TAPPI).

[6] National Center for Biotechnology Information (2024). PubChem Compound Summary for CID 61655, Lead perchlorate. Retrieved October 15, 2024 from <https://pubchem.ncbi.nlm.nih.gov/compound/Lead-perchlorate>

[7] B. Magnusson and U. Örnemark (eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics, (2nd ed. 2014). ISBN 978-91-87461-59-0. Available from <http://www.eurachem.org>

[8] Svenska institutet för standarder. (1994). *Hydrogen sulphide ion concentration* (SCAN-N 31:94). <https://www.sis.se/contentassets/34e8e2d3bd5f43c7a9ee7ce4715cd59c/scan-n-3194-en.pdf>

[9] Svenska institutet för standarder. (1983). *Total sulphur* (SCAN-N 5:83). <https://www.sis.se/contentassets/34e8e2d3bd5f43c7a9ee7ce4715cd59c/scan-n-583-en.pdf>

[10] Svenska institutet för standarder. (1985). *Suphate content* (SCAN-N 6:85). <https://www.sis.se/contentassets/34e8e2d3bd5f43c7a9ee7ce4715cd59c/scan-n-685-en.pdf>

8 Appendix

8.1 Raw data

RD 1: Raw data of measurements with a 0,099 g/L Na₂SO₄ standard solution for the determination of LOD and LOQ for the formaldehyde method. The table shows run number and resulting concentration in g SO₄²⁻/L.

1	2	3	4	5	6	7	8	9	10	11
0,15	0,18	0,19	0,19	0,14	0,14	0,15	0,14	0,14	0,14	0,14

RD 2: Raw data for the determination of the linear range for the formaldehyde method. Concentrations in g SO₄²⁻/l. (Uneven stock solution concentrations due to a miscalculation.)

	0,99	2,97	5,94	8,91	11,88	14,84
1	1,01	2,94	5,81	8,75	11,78	14,72
2	1,01	2,94	5,84	8,78	11,80	14,74
3	1,00	2,94	5,83	8,81	11,77	14,72

4	1,01	2,94	5,85	8,82	11,78	14,72
5	1,00	2,94	5,86	8,83	11,76	14,82

RD 3: Raw data for the determination of precision and trueness for the formaldehyde method.
Concentrations in g SO₄²⁻/l.

	2	5
1	2,00	4,99
2	2,00	4,99
3	2,00	4,97
4	2,00	4,99
5	2,00	4,98
6	2,00	4,97
7	1,99	4,97
8	2,00	4,97
9	1,99	4,98
10	1,99	4,97
11	1,99	4,97

RD 4: Blank measurement raw data for the determination of LOD and LOQ for thermometric titration. The table shows run number and resulting concentration in g SO₄²⁻/l.

1	2	3	4	5	6	7	8	9	10	11
0,10	0,10	0,13	0,16	0,13	0,10	0,06	0,13	0,19	0,19	0,26

RD 5: Raw data for the determination of the linear range for thermometric titration. Concentrations in g SO₄²⁻/l. (Uneven stock solution concentrations due to a miscalculation.)

	0,99	2,97	5,94	8,91	11,88	14,84
1	1,12	2,88	5,22	7,75	10,21	12,17
2	1,12	2,88	5,28	7,85	10,31	12,68
3	1,15	2,82	5,32	7,88	10,37	12,71

4	1,12	2,79	5,32	7,75	10,25	12,68
5	1,15	2,79	5,32	7,85	10,25	12,62

RD 6: Raw data for the determination of precision and trueness for thermometric titration. Concentrations in g SO₄²⁻/l.

	2	5
1	1,92	4,51
2	1,89	4,61
3	1,92	4,61
4	1,95	4,55
5	1,92	4,55
6	2,02	4,51
7	1,99	4,55
8	1,95	4,58
9	1,99	4,51
10	2,02	4,51
11	1,99	4,61

RD 7: Sulfate results for white liquor for all methods used in the general comparison.

Day	Total S (g/L)	HS ⁻ (g S/L)	SO ₄ ²⁻ (g/L) Total S*	SO ₄ ²⁻ (g/L) Formaldehyde	SO ₄ ²⁻ (g/L) Thermometric titration
1	25,25	22,30	8,84	3,28	3,68
2	25,29	22,48	8,42	3,31	3,68
3	25,35	23,10	6,74	3,87	4,03
4	25,42	22,39	9,08	3,62	4,10
5	26,26	23,16	9,29	4,10	4,48
6	27,15	23,72	10,28	4,25	4,45
7	27,18	23,32	11,57	3,95	4,29
8	27,27	23,26	12,01	5,85	6,50

9	27,25	23,69	10,67	3,50	3,75
10	27,22	23,29	11,78	3,13	3,33
11	29,12	24,05	15,19	6,60	7,40
12	29,19	22,80	19,15	6,45	6,85
13	27,33	22,75	13,72	5,75	6,24
14	28,16	23,57	13,75	5,32	5,92
15	28,10	24,26	10,91	5,30	5,41
16	27,48	24,67	8,42	4,42	4,74
17	27,85	23,54	12,91	6,21	6,50
18	26,89	21,37	16,54	11,12	11,50
19	28,00	24,47	10,58	4,46	4,10
20	28,36	24,50	11,57	4,32	3,94

RD 8: Sulfate results for green liquor for all methods used in the general comparison.

Day	Total S (g/L)	HS ⁻ (g S/l)	SO ₄ ²⁻ (g/L) Total S*	SO ₄ ²⁻ (g/L) Formaldehyde	SO ₄ ²⁻ (g/L) Thermometric titration
1	25,34	23,13	6,62	3,62	3,39
2	23,97	22,73	3,72	2,41	1,86
3	23,50	21,81	5,06	3,02	2,50
4	25,31	22,95	7,07	3,48	3,07
5	25,06	22,64	7,25	3,50	3,01
6	25,89	23,37	7,55	3,56	3,20
7	26,24	23,30	8,81	4,35	4,07
8	26,63	24,25	7,13	3,33	2,88
9	27,12	24,50	7,85	3,32	2,79
10	26,07	24,26	5,42	1,53	0,74
11	27,29	23,48	11,42	5,92	6,02
12	26,36	22,37	11,66	5,30	5,16

13	26,66	22,81	11,54	5,69	5,67
14	27,31	23,54	11,30	5,61	5,48
15	27,10	24,12	8,93	4,26	3,91
16	27,34	23,29	12,13	8,21	8,45
17	27,73	24,45	9,83	4,79	4,58
18	28,03	24,65	10,13	6,02	5,99
19	26,69	23,44	9,74	4,68	4,29
20	27,30	24,47	8,48	3,00	2,08

RD 9: White liquor reduction degree results measured using the total sulfur method and the thermometric titration.

Day	Total sulfur reduction degree (%)	Thermometric titration reduction degree (%)
1	88,3	94,8
2	88,9	94,8
3	91,1	94,5
4	88,1	94,2
5	88,2	93,9
6	87,4	94,1
7	85,8	94,2
8	85,3	91,5
9	86,9	95,0
10	85,6	95,4
11	82,6	90,7
12	78,1	90,9
13	83,2	91,6
14	83,7	92,3
15	87,0	93,1
16	89,8	94,0

17	84,5	91,6
18	79,5	84,8
19	87,4	94,7
20	86,4	94,9

RD 10: Green liquor reduction degree results measured using the total sulfur method and the thermometric titration.

Day	Total sulfur reduction degree (%)	Thermometric titration reduction degree (%)
1	91,3	95,3
2	94,8	97,3
3	92,8	96,3
4	90,7	95,7
5	90,3	95,8
6	90,3	95,6
7	88,8	94,5
8	91,1	96,2
9	90,3	96,3
10	93,1	99,0
11	86,0	92,1
12	84,9	92,9
13	85,6	92,3
14	86,2	92,8
15	89,0	94,9
16	85,2	89,2
17	88,2	94,1
18	87,9	92,5
19	87,8	94,2
20	89,6	97,2

RD 11: Raw data from Alkali R green liquor analysis. Concentrations are expressed as grams of NaOH per liter.

Day	Alkali R Na ₂ S	Alkali R Na ₂ SO ₄
1	57,58	4,82
2	55,46	4,11
3	57,57	3,95
4	60,06	4,61
5	58,79	3,10
6	55,06	6,03
7	59,95	3,85
8	57,35	4,67
9	58,56	3,52
10	58,47	2,05

RD 12: Green liquor sulfate analysis results. (Day 11-20 in previous tables.) The raw data for the Alkali R results can be found in RD 11.

Day	SO ₄ ²⁻ (g/L) Formaldehyde	SO ₄ ²⁻ (g/L) Thermometric titration	SO ₄ ²⁻ (g/L) Alkali R
1	5,92	6,02	5,79
2	5,30	5,16	4,94
3	5,69	5,67	4,74
4	5,61	5,48	5,54
5	4,26	3,91	3,72
6	8,21	8,45	7,24
7	4,79	4,58	4,62
8	6,02	5,99	5,61
9	4,68	4,29	4,23
10	3,00	2,08	2,46

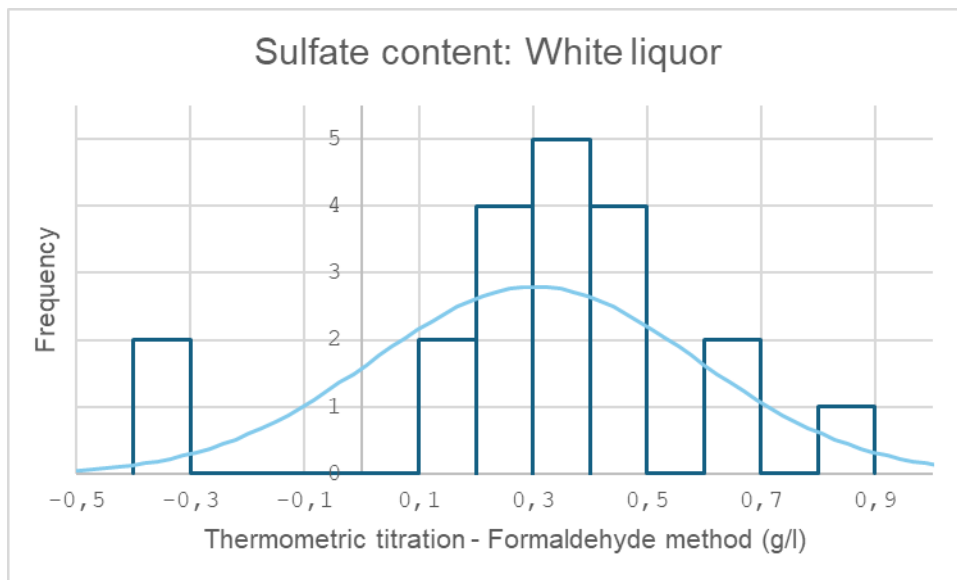
RD 13: Green liquor reduction degree results. (Day 11-20 in previous tables.)

Day	Total sulfur reduction degree (%)	Thermometric titration reduction degree (%)	Alkali R reduction degree (%)
1	86,0	92,1	92,20
2	84,9	92,9	93,10
3	85,6	92,3	93,51
4	86,2	92,8	92,44
5	89,0	94,9	95,00
6	85,2	89,2	90,32
7	88,2	94,1	93,74
8	87,9	92,5	92,47
9	87,8	94,2	94,34
10	89,6	97,2	96,65

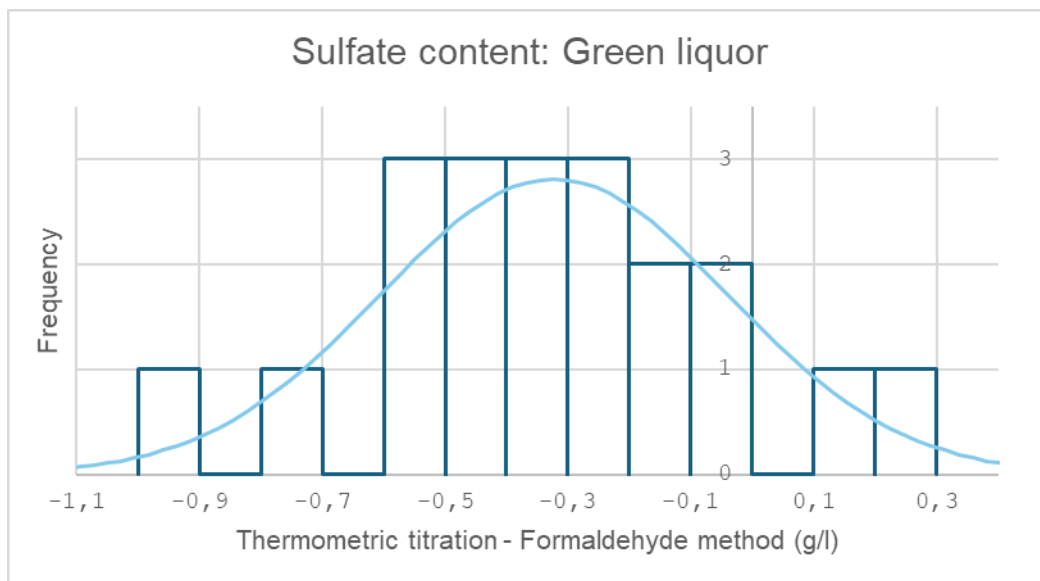
RD 14: Green liquor total sulfur results. (Day 11-20 in previous tables.) The raw data for the Alkali R results can be found in RD 11.

Day	Total S (g/L)	Alkali R total S (g/L)	Difference (Total S-Alkali R)
1	27,29	25,01	2,28
2	26,36	23,87	2,49
3	26,66	24,65	2,01
4	27,31	25,92	1,39
5	27,10	24,80	2,30
6	27,34	24,48	2,86
7	27,73	25,57	2,16
8	28,03	24,81	3,22
9	26,69	24,84	1,85
10	27,30	24,21	3,09

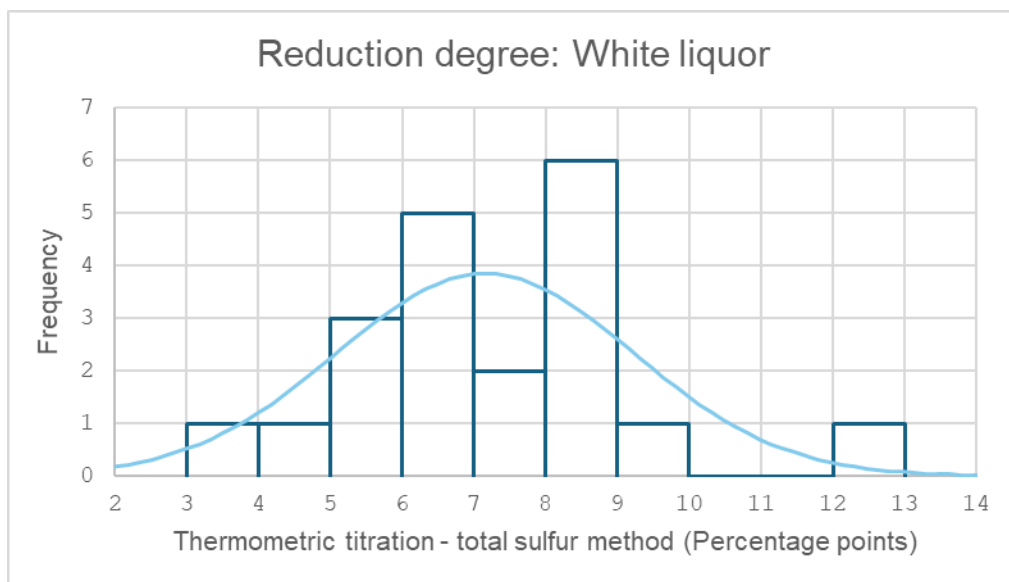
8.2 Histograms



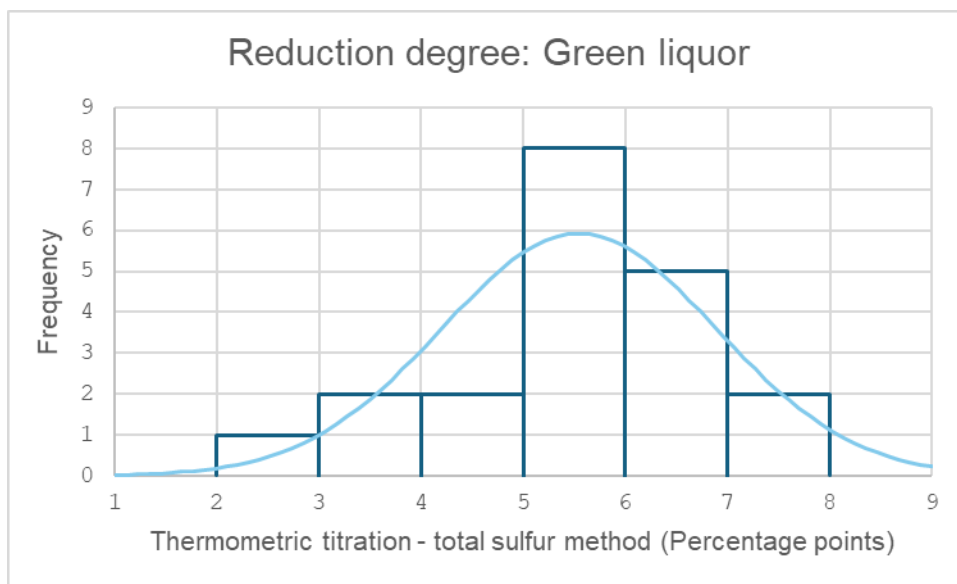
Histogram 1: The distribution of the sulfate content differences between the thermometric titration and the formaldehyde method for white liquor analysis.



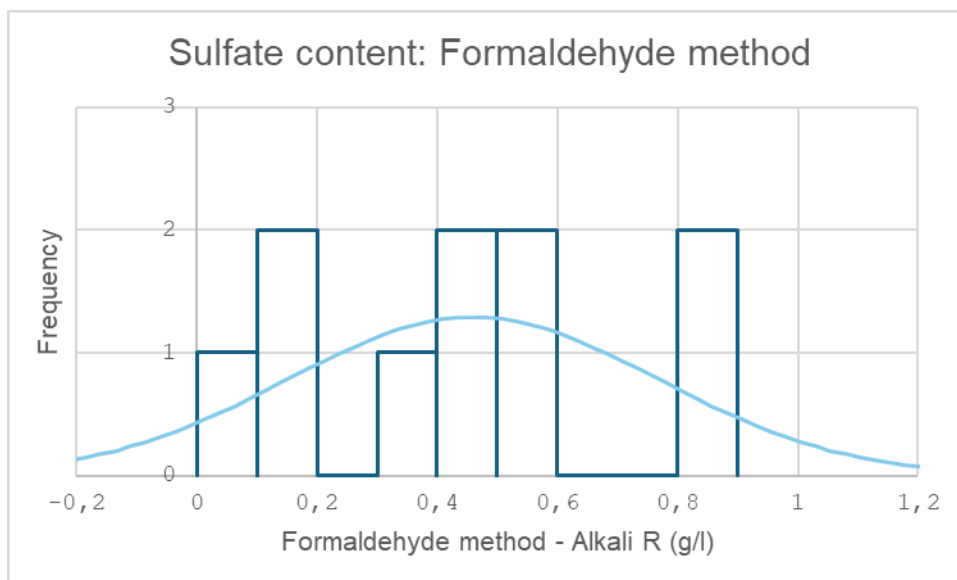
Histogram 2: The distribution of the sulfate content differences between the thermometric titration and the formaldehyde method for green liquor analysis.



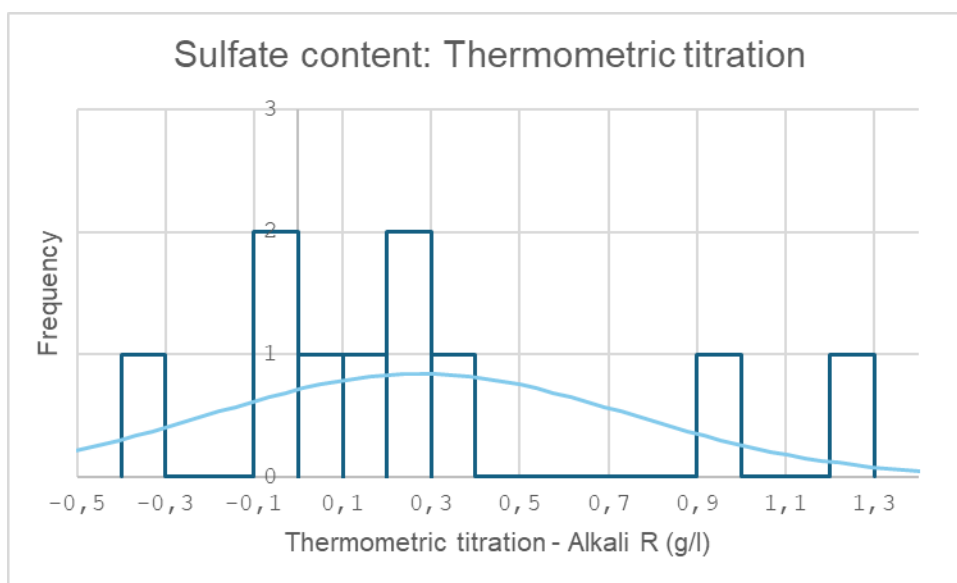
Histogram 3: The distribution of the reduction degree differences between the thermometric titration and the total sulfur method for white liquor analysis.



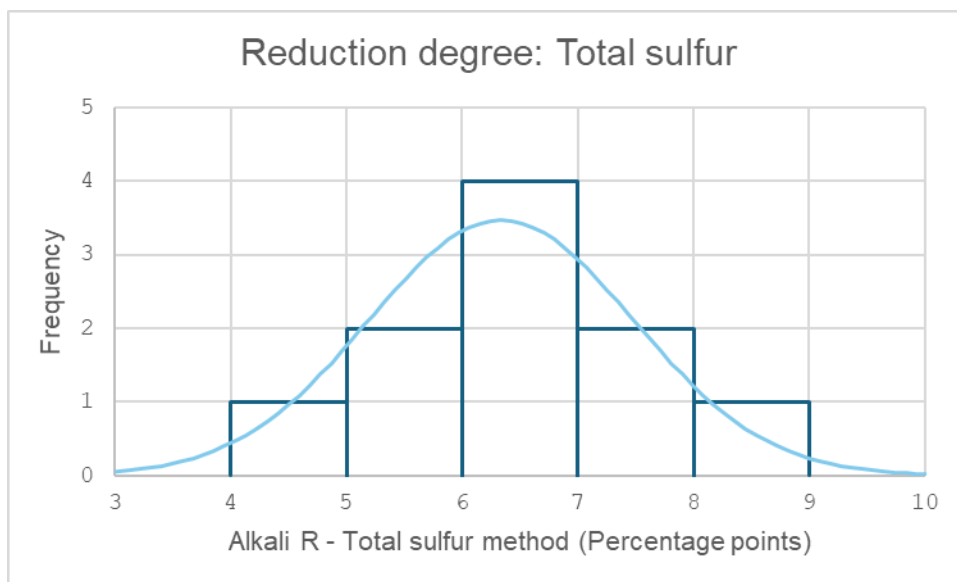
Histogram 4: The distribution of the reduction degree differences between the thermometric titration and the total sulfur method for green liquor analysis.



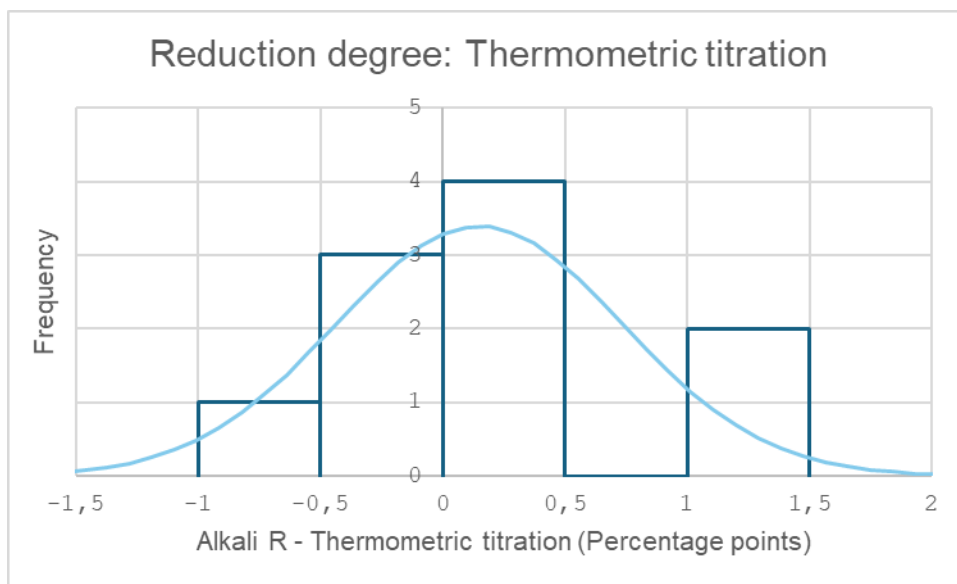
Histogram 5: The distribution of the sulfate content differences between the formaldehyde method and Alkali R for green liquor analysis.



Histogram 6: The distribution of the sulfate content differences between the thermometric titration and Alkali R for green liquor analysis.



Histogram 7: The distribution of the reduction degree differences between the total sulfur method and Alkali R for green liquor analysis.



Histogram 8: The distribution of the reduction degree differences between the thermometric titration and Alkali R for green liquor analysis.