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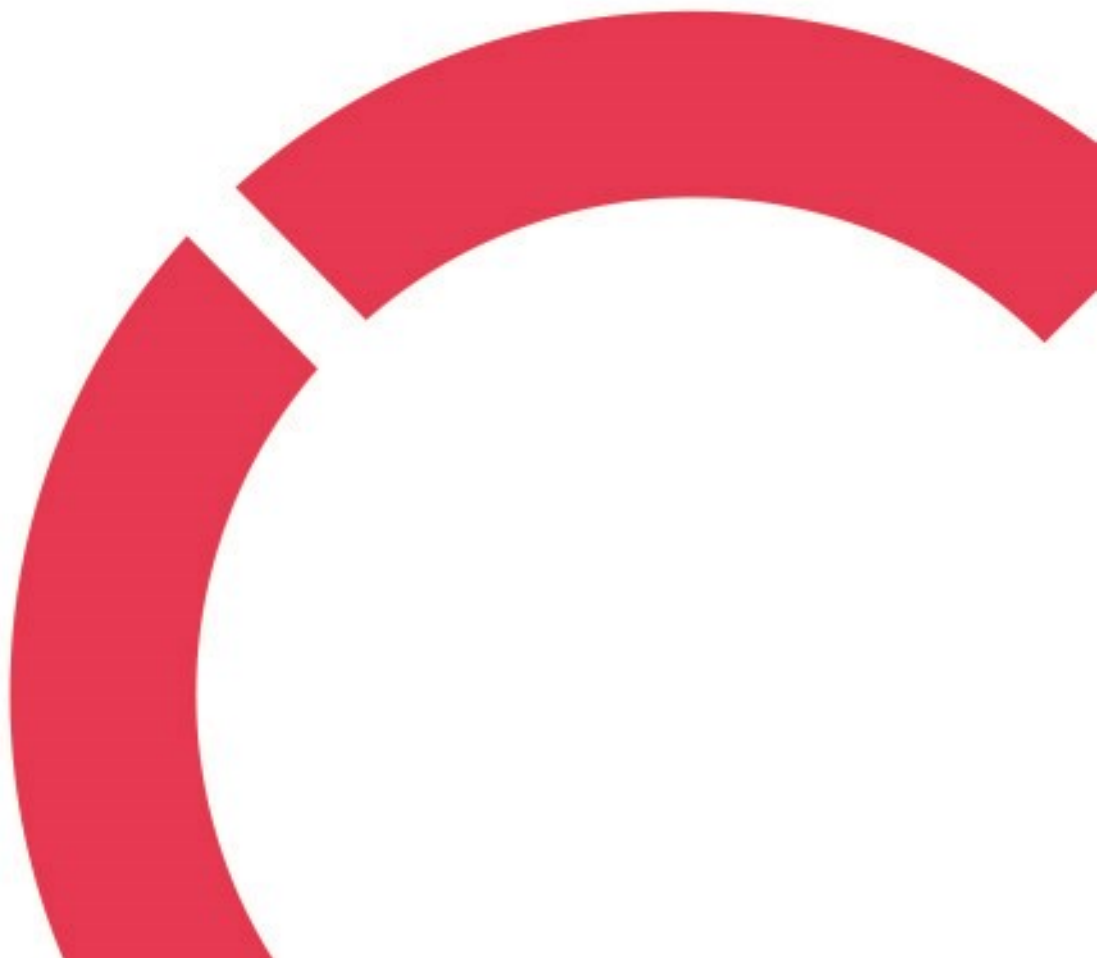
**COLOUR MEASUREMENT OF METAL HYDROXIDE SAMPLES
AND CORRELATION WITH OXIDATION STATE**

Thesis

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ABSTRACT

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Name of thesis COLOUR MEASUREMENT OF METAL HYDROXIDE SAMPLES AND CORRELATION WITH OXIDATION STATE		
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<p>A client company felt the need to research a faster way to measure oxidation states of rapidly oxidizing metal hydroxide samples. The used method of analysis was slow and the average oxidations state could change during the long process as the samples were exposed to ambient oxygen. Fast colour measurement in the wavelength range of visible light was considered a candidate for a new analysis method, as the sample visibly changed colour as it oxidized. For the duration of the practical part, a spectrophotometer designed for colour measurement was acquired for trial use in the research laboratory, the test run of which was performed as part of this thesis.</p> <p>In this thesis a suitable preparation method was also developed for the research samples by experimenting with different methods and choosing a suitable combination from them. The colour of the samples was analysed with the spectrophotometer, and untreated parallel samples were sent to the analysis laboratory for the determination of the average oxidation state. The colour and average oxidation state of the samples were statistically compared and an attempt was made to find a correlation between the colour and the oxidation state. The results were promising, but unclear because the device was only in trial use for a month and there was no time to get enough measurements. There were also not enough oxidized samples for the measurements.</p> <p>Portions of this thesis are covered by a nondisclosure agreement and information has been purposefully obfuscated or left out of the public edition. The results as a whole have been handed over to the client company as a confidential appendix.</p>		

Key words colour measurement, metal hydroxide, oxidation state, spectrophotometer, spectrophotometry, visible light wavelength
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TIIVISTELMÄ OPINNÄYTETYÖSTÄ

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Koulutus Kemiantekniikka		
Työn nimi METALLIHYDROKSIDINÄYTTEIDEN VÄRINMITTAUS JA KORRELAATIO HAPETUSASTEeseen		
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<p>Toimeksiantajayrityksellä ilmeni tarve kehittää uutta, nopeampaa tapaa mitata hapetusasteita nopeasti hapettuvista metallihydroksidinäytteistä. Käytetty analyysimenetelmä oli hidas, ja keskimääräinen hapetusaste saattoi muuttua pitkän prosessin aikana, kun näytteet altistuivat ilmakehän hapelle. Nopeaa värinmittausta näkyvän valon aallonpituuden alueella ehdotettiin uudeksi analyysimenetelmäksi, sillä näyte muutti näkyvästi väriä hapettuessaan. Työn ajaksi tutkimuslaboratorioon hankittiin koekäyttöön värinmittaukseen suunniteltu spektrofotometri, jonka koeajo suoritettiin osana tätä opinnäytetyötä.</p> <p>Tässä opinnäytetyössä tutkimusnäytteille kehitettiin myös soveltuva esikäsittelymenetelmä kokeilemalla erilaisia menetelmiä ja valitsemalla niistä soveltuva yhdistelmä. Näytteiden väri analysoitiin koekäytössä olevalla spektrofotometrillä ja käsittelemättömät rinnakkaisnäytteet lähetettiin analyysilaboratorioon keskimääräisen hapetusasteen määrittämiseksi. Näytteiden väriä ja hapetusastetta vertailtiin tilastollisesti ja pyrittiin löytämään korrelaatio värin ja hapetusasteen välille. Tulokset olivat lupaavia mutta epäselviä, sillä laite oli koekäytössä vain kuukauden ja mittauksia ei ehditty saada riittävästi. Mittauksiin ei myöskään sisältänyt tarpeeksi hapettuneita näytteitä.</p> <p>Osa tästä opinnäytetyöstä on salassapitosopimuksen kattamaa ja täten osa tiedosta on tarkoituksellisesti jätetty pois julkisesta versiosta. Tulokset kokonaisuudessaan on luovutettu toimeksiantajayritykselle erillisenä liitteenä.</p>		
Asiasanat värinmittaus, metallihydroksidi, hapetusaste, spektrofotometri, spektrofotometria, näkyvän valon aallonpituus		

CONCEPT DEFINITIONS

CIE

Commission Internationale de l'Eclairage, International Commission on Illumination

CIELAB 1976

Colour space defined by the International Commission on Illumination in 1976

D50 particle size

Average particle size. 50% of particles are smaller and 50% larger than the indicated value.

L*, a* and b*

Colour values used by the CIELAB 1976 uniform colour scale

RAL

Reichs-Ausschuß für Lieferbedingungen und Gütesicherung, National Commission for Delivery Terms and Quality Assurance

RAL K7 Classic

A collection of 216 colours.

UV

Ultraviolet light spectrum, 200 – 380 nm

VIS

Visible light spectrum, 380 – 780 nm

VS3200

MetaVue VS3200 Color Matcher Benchtop Spectrophotometer

ABSTRACT
CONCEPT DEFINITIONS
CONTENTS

1 INTRODUCTION.....	1
2 THEORETICAL BACKGROUND	2
2.1 Oxidation state and correlation with the colour of metal ions.....	2
2.2 Spectrophotometers	2
2.3 Colour and colorimetry	3
2.4 Colour measurement with the VS3200 and CIELAB 1976.....	3
2.5 Sample handling and preparation	4
3 PREPARATION METHODS AND MEASUREMENTS	6
3.1 Sampling.....	7
3.2 Sample preparation methods	7
3.3 Colour measurement.....	8
3.4 Behaviour of the sample with the chosen preparation method.....	9
4 RESULTS	10
4.1 Sample preparation methods	10
4.1.1 Decanting	11
4.1.2 Filtering and washing	12
4.1.3 Effect of moisture content on colour measurement.....	13
4.1.4 Drying	16
4.1.5 Antioxidants	16
4.2 Optimized preparation method and variables affecting colour measurement.....	19
4.3 Behaviour of the sample with the chosen preparation method.....	19
4.4 Oxidation states and correlation with colour of the sample.....	20
5 CONCLUSIONS	23
REFERENCES.....	24

FIGURES

FIGURE 1. CIELAB colour chart with a measurement point as displayed by VS3200	4
FIGURE 2. Settling time graph for five different samples	11
FIGURE 3. Effect of the sample's moisture content	15
FIGURE 4. Effect of ascorbic acid	17
FIGURE 5. Effect of time in ambient air	18
FIGURE 6. Correlation between average oxidation state and the three colour values.....	21
FIGURE 7. Correlation between D50 particle size and a* value	22

PICTURES

PICTURE 1. Picture taken by VS3200 of the sample while measuring.....	5
PICTURE 2. Separated liquid phase and reflections	10
PICTURE 3. Filtered and washed samples.	13
PICTURE 4. Effect of moisture content	14
PICTURE 5. Effect of moisture content	14

TABLES

TABLE 1. Overview of experiments done during the thesis.....6
TABLE 2. Overview of the preparation methods used.....8
TABLE 3. Oxidized samples with parallel unoxidized samples.20

1 INTRODUCTION

The client company was measuring average oxidation state of metal ions from heterogenous samples. The samples included a solid and a liquid phase. The solid phase was completely opaque and the liquid phase exhibited variability in transparency across distinct samples once separated. Both phases darkened from bright to darker colours when exposed to ambient air or gaseous oxygen. The current method for analyzing the average oxidation states of the metal ions in the sample exposed the samples to oxygen in air or dissolved into solutions, leading to unreliable results. Research was begun to search for a correlation between the colour and the average oxidation state of the ions in the sample. During the practical part of the thesis, the ratio of the metals in the samples did not change.

Before this thesis a RAL K7 colour map was used to compare sample colours by eye. The map was not objective or provide enough colour choices to accurately depict the changes in the samples' solid component's colour. Every person interpreted the colours differently and ambient lighting conditions changed during the working day. An X-rite MetaVue VS3200 Color Matcher Benchtop Spectrophotometer was acquired for trial use, which operated in the visible light spectrum of 400-700 nm. It could quickly and objectively measure the colour of a sample, minimizing the sample's contact with oxygen. A single measurement took under ten seconds to complete. The device was rented for a month as a trial for a possible purchase, which limited the number of trials completed, which made it more difficult to draw initial conclusions.

A correlation between the colour of the sample and its average oxidation state was searched for. This thesis included device trialling in addition to the actual research tasks. Only a part of research for a new analysis method was included, ignoring phases such as validation. The first research task was finding a suitable preparation method for the samples. The preparation method was to be quick and give consistent results. The sample had to have minimal contact with oxygen to preserve its colour which measurably changed within seconds of exposure to air. The second task was to find out how quickly the samples oxidized with the chosen preparation methods. The third task was to search for a correlation between the colour of the solid phase and the oxidation state of the metal ions in it. Parallel samples were sent to an analytical laboratory where the average oxidations state of the metal ions was measured.

2 THEORETICAL BACKGROUND

The theory for this thesis relied mainly on basic information regarding the various subject that formed the foundation for the experiments, such as training material from X-rite, CIE standards and various books and articles on chemistry and colour. Research articles concerning colour analysis of opaque metal compound slurries with visible light wavelengths was not found during the research step. Most closely related articles were from water treatment, where minuscule amounts of metals in transparent solutions were coloured using additives and then analysed with a spectrophotometer (Zhao & Zhang 2017, 1084.) The samples under research in this thesis were highly concentrated and heterogenous with a solid phase. It was inferred that solid metal compounds are rarely measured using absorption of visible light wavelengths.

2.1 Oxidation state and correlation with the colour of metal ions

Oxidation state, used synonymously with oxidation number, describes the number of electrons an atom has gained, lost or otherwise appears to use in bonding with another atom. As electrons have a negative charge, an atom that has gained an electron has an oxidation state of -1, and an atom that has lost an electron has a state of +1. (Bissonnette, Madura, Herring & Petrucci 2011, 84.) Metal ions can have a variety of oxidations states and these ions can display a range of colours. For example, Vanadium ions in a solution display a yellow colour in the +5 oxidation state, blue in +4 state, green in +3 state and violet in +2 state. (Bissonnette et al. 2011, 1047.) The samples analysed during the practical phase of this thesis darkened and changed colour from green to brown as they were oxidized, indicating a similar correlation.

2.2 Spectrophotometers

Spectrophotometers are scientific instruments which measure chemical concentrations using electromagnetic waves. The procedure is called spectrophotometry. According to Beer's law, concentration of a species and its absorbance of electromagnetic waves are directly proportional, which allows measurement of chemical concentrations (Harris & Lucy 1999, 511 – 515.) Spectrophotometer can use the emission, transmission, interference or absorption of light from the sample to analyze it (Kuehni 2012, 5 – 6;

Niiranen & Jaarinen 2008 ,48 – 50). Inorganic analysis uses spectrophotometry in the ultraviolet and visible light spectrum, ranging from 200 – 380 nm for ultraviolet light and 380 – 780 nm for visible light spectrum (Marczenko & Balcerzak 2000, 26.) The VS3200 spectrophotometer uses visible light wavelengths of 400 – 700 nm and absorption of light to analyze samples (Kuehni 2012, 5; Wakeford 2023).

2.3 Colour and colorimetry

Light consists of a range of electromagnetic radiation. Wavelengths from around 380 to 780 nanometers are light that human's eyes are sensitive to, and are referred to as visible light or visible spectrum (Kuehni 2012, 4 – 5; Marczenko & Balcerzak 2000, 26). Colorimetry is used to quantitate and describe the human colour vision (Ohno 2000, 1). The term has been used for an analytical method developed in the middle of the 19th century, where the colour of an unknown chemical element sample was compared to a standard (Marczenko & Balcerzak 2000, 26.) Colours do not exist in the scientific sense, as they are experienced and judged by an individual. For example, the yellowness of the individual experience caused by light with a wavelength of 575 nm cannot be defined. (Kuehni 2012, 24 – 25.) However, a machine can analyze the spectrum without human interference (Wakeford 2023).

Many variables still affect the colour of samples. For powder, it was identified that the transparency and grain size of the substance, the nature of solvents used and light intensity were key factors affecting the colour of the powder (Zheng et al. 2020, 7).

2.4 Colour measurement with the VS3200 and CIELAB 1976

Electromagnetic waves used by the X-rite MetaVue VS3200 are of the visible light wavelength, 400 – 700 nm, which can be seen as colour. VS3200 functions using CIE 1976, or CIELAB uniform colour scale, which uses three values to describe colour. They are L*, a* and b*. L* defines lightness, a* the red/green value and b* yellow/blue value. The a*- and b*-values range from -100 to 100, and L*-value from 0 to 100. (Ohno 2000, 3; Kuehni 2012, 5; X-Rite 2016, 11.)

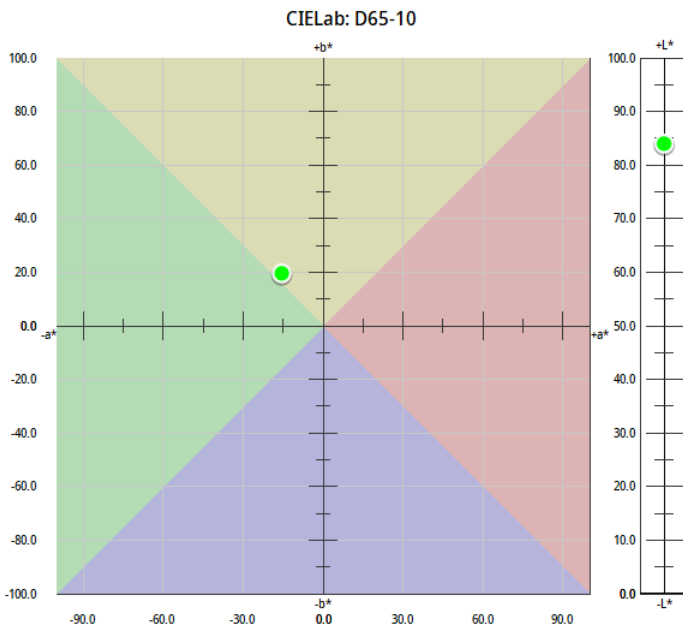


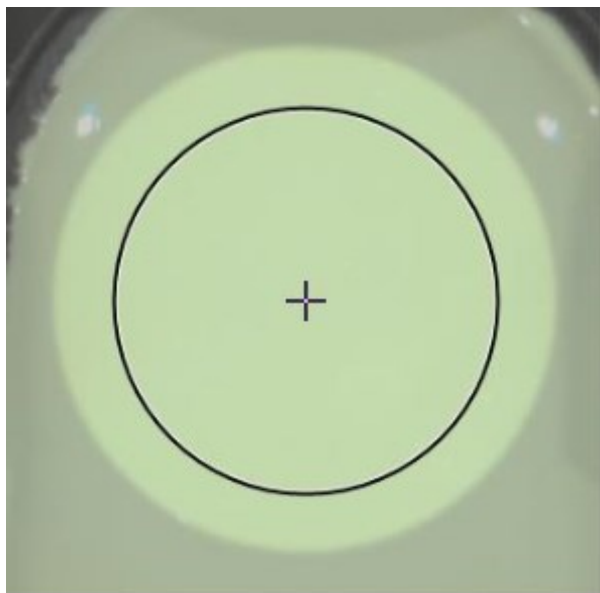
FIGURE 1. CIELAB colour chart with a measurement result as displayed by VS3200 spectrophotometer

In a colour diagram shown by the VS3200 (FIGURE 1.) the a^* axis is from left to right, with the positive values trending towards red from green. From bottom to top, the b^* axis trends towards yellow from blue. The L^* axis depicts lightness, with a value of 0 being black and 100 a perfect white. The centre of the a^*b^* -plane is grey. A measurement of a sample is visible (PICTURE 1.) on the diagram (FIGURE 1.), with the L^* axis being displayed on the right side. This measurement had the values of $L^* = 84,06$, $a^* = -15,58$ and $b^* = 19,68$. The instrument has an error of $\pm 0,04$. D65-10 refers to the light source and sensor used. “D65” is a CIE standard illuminant representing daylight with a colour temperature of 6500K. The “-10” refers to a CIE 1964 supplementary standard colorimetric observer with a field of view of 10° . (Ohno 2000, 2 – 4).

2.5 Sample handling and preparation

In order to achieve a reliable result, five phases must be successfully completed. They are sampling, sample storage, sample preparation, analysis and interpretation of results. (Suomi 2009, 10.) The process of collecting a representative bulk sample for analysis is called sampling. Sampling heterogenous samples is best done from a turbulent flow. The samples generally require preparation for analysis to remove interfering substance or to change the sample to more suitable form of a laboratory sample for the chosen analysis method or instrument. (Harris & Lucy 1999, 10; Harris & Lucy 1999, 817; Suomi 2009, 10). Badly prepared or unprepared samples can affect the analysis, interpretation of results or even damage

the instruments (Suomi 2009, 10). The samples in this thesis are not stored for extended periods of time since they are sensitive to oxidation, and are prepared and analyzed immediately in the majority of cases.



PICTURE 1. Picture taken by VS3200 spectrophotometer of the sample while measuring.

3 PREPARATION METHODS AND MEASUREMENTS

An overview of the experiments conducted can be found (TABLE 1) in order by date. The purpose of the experiments was to answer the first two research questions. The first question was to find a suitable preparation method and the second question was to find out how quickly the samples oxidized with the chosen preparation methods. Experiments from Settling 1 until Filtering 4 (TABLE 1, shaded orange) were to choose the preparation method and the following (TABLE 1, shaded blue) colour measurements and oxidation tests were to observe the behaviour of the samples and to collect enough measurement data to find a correlation between the average oxidation state of the sample and its colour.

TABLE 1. Overview of experiments conducted during the thesis.

Experiment	Overview
Settling 1	Experiment on decanting the sample.
Settling 2	Further experiments on decanting the sample.
Filtering 1	Initial filtering test with different filter times.
Filtering 2	Filtering test including washing steps.
Filtering and colour measurement 1	Filtering test including colour measurement of samples with varying moisture content.
Filtering and colour measurement 2	Samples with varying moisture content and a coloured base solution.
Filtering and colour measurement 3	Samples with varying moisture content. Variations included ion exchanged water, a coloured base solution or a scraped cake surface layer.
Filtering and colour measurement 4	Included an unfiltered sample. Sample was treated with ascorbic acid and measured colour change over time in parallel with an untreated sample.
Colour measurements 1 & 2	Used the finalized preparation method to treat a sample and measured colour from it. A parallel sample was sent to another laboratory for the measurement of average oxidation state.
Colour measurement 3 & 4	It was attempted to purposefully oxidize parallel samples by leaving them in open containers overnight in addition to colour measurement.

Colour measurement 5 – 8	Regular colour measurement. See Colour measurement 1 & 2.
Oxidation experiment 1 – 3	In addition to regular colour measurement, a parallel samples were oxidized with pure oxygen gas.

3.1 Sampling

The majority of the samples were taken from the process at set intervals using the client's normal sampling method. The sample was taken with a 60 ml syringe using an integrated sampling pipeline. These samples were taken from turbulent flow, as recommended in chapter 2.5. In addition, some samples were taken from completed batches that were stored in large plastic containers, which were mixed using a mixer. The sample was taken with a 60 ml syringe from the container immediately after mixing.

3.2 Sample preparation methods

The first research task was to find a suitable way to prepare the samples for colour measurement. This was conducted experimentally by solving problems noticed and adjusting the preparation methods as necessary on a trial-by-error basis. The preparation method should expose the sample to oxygen as little as possible, as it oxidizes readily in ambient oxygen. The existing preparation method consisted of washing the sample with a sodium hydroxide solution and ion exchanged water during filtration, drying the sample in a vacuum oven after filtering and storing it in a foil bag purged with nitrogen gas. Once removed from the vacuum oven, the sample rapidly oxidized and its surface colour changed to near black. The sample was then sent to an analytical laboratory in the purged foil bag for average oxidation state measurement.

The samples taken from the process were immediately ready for measurements or treatments. The samples were pale-coloured green to beige solutions with a fine grained coloured solid phase and a clear or slightly opaque coloured liquid phase. The colour of the solid phase was the object of measurement. An overview of the different preparation methods used has been provided (TABLE 2).

TABLE 2. Overview of the preparation methods used.

Preparation method	description
No preparation	Sample was inserted into the measurement spoon of the spectrophotometer straight from the manufacturing process.
Settling and decanting	Sample was left to gravitationally separate in a closed sample tube and the liquid phase was decanted. Solid phase was inserted into the sampling spoon.
Filtering	Sample was filtered with a Büchner funnel and a paper filter until liquid phase had been removed, as quickly as possible, and some of the solid was inserted into the sampling spoon.
Filtering with an antioxidant	Ascorbic acid was added into the sampling tube before sampling. Sample was mixed by hand with the antioxidant in the sampling syringe before filtering.
Drying	Sample was filtered and dried in an oven before measurement.

3.3 Colour measurement

The MetaVue VS3200 Spectrophotometer was easy to use, requiring no installation other than software on a computer and connecting the cables. The installation process was guided and laboratory personnel trained by the manufacturer's representative remotely. The instrument had an integrated white calibration slider and a secondary green colour standard to check for errors. The instrument was cleaned and calibrated with its integrated, automatic calibration mode daily before any measurements. A measurement took between eight and ten seconds. The sample was placed into sample dish and slid under the instrument and the measurement was taken with the press of a button. The device had the capability to automatically average several consecutive measurements, and it was decided to use this feature to reduce the effect user error.

3.4 Behaviour of the sample with the chosen preparation method

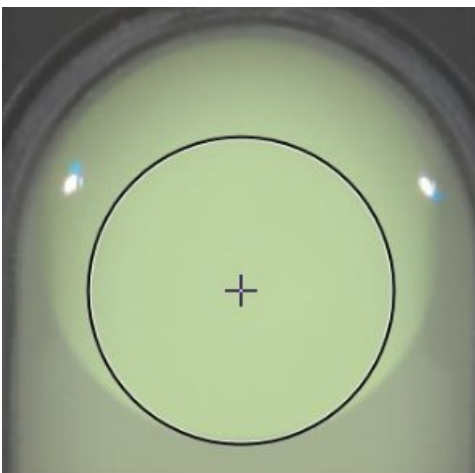
The second research task was to determine how the sample behaved with the chosen preparation method. An optimized sample preparation method was developed based on the experiments explained in chapter 3.2. The completed preparation method can be found in chapter 4, Results. To answer the second research question, three samples were colour measured automatically every three minutes over a longer period of time to see how their colour changed over time. The measurement time ranged from 57 to 84 minutes depending on the instrument's availability. The samples were mixed after the long measurement series and colour measured again. The results of all experiments in chapter 3 were compiled and statistically analysed utilizing Microsoft Office 365 Excel application.

4 RESULTS

The research and experimenting on this thesis was split into three parts, as with the research tasks. The first part consisted of testing the different preparation methods and choosing the preparation method. The second part was measuring colour and determining how the samples behaved with the chosen preparation method. The third part was analysing and processing the results to search for a correlation between the colour of the sample and its average oxidation state (Isosaari 2023).

4.1 Sample preparation methods

The first preparation method used was to not use any preparations and simply measure colour straight from the sample. This was the fastest available method, but the spectrophotometer could not reliably measure colour of the sediment through the quickly separating liquid phase layer. The VS3200 spectrophotometer can be set to take a picture of any measurements taken. The separating layer caused a shadow around the edges of the measurement spoon and darkened the colour of the sample overall. The liquid phase also caused strong, visible reflections from the spectrophotometer's light source like with the next methods used, decanting. These effects could be reduced by shrinking the measurement area of the VS3200, marked as a black ring with a cross at the centre. (PICTURE 2).



PICTURE 2. Separated liquid phase and bright reflection spots from a decanted sample.

4.1.1 Decanting

The second method was to let the solid phase gravitationally separate from the liquid phase in a closed 50 ml sampling tube and decant the liquid phase as much as possible and pour the leftover sample into a measurement dish. This will be referred to as settling. Even the fastest solid phase to settle adequately took over 50 minutes in the 50 ml sample containers (FIGURE 2). It was decided that it was not realistic in large scale to have possibly dozens of samples settling at the same time. The sampling tubes were not airtight and some surface discoloration was observed over the long settling time. Some problems of phase separation and reflections persisted with colour measurement as with no preparation. (PICTURE 2). There was also concern for the error caused by a varying refractive index of the solution and the change in refractive index as light was reflected through the liquid phase. Refractive index and its possible changes or effects were not measured as it was decided to remove the liquid phase.

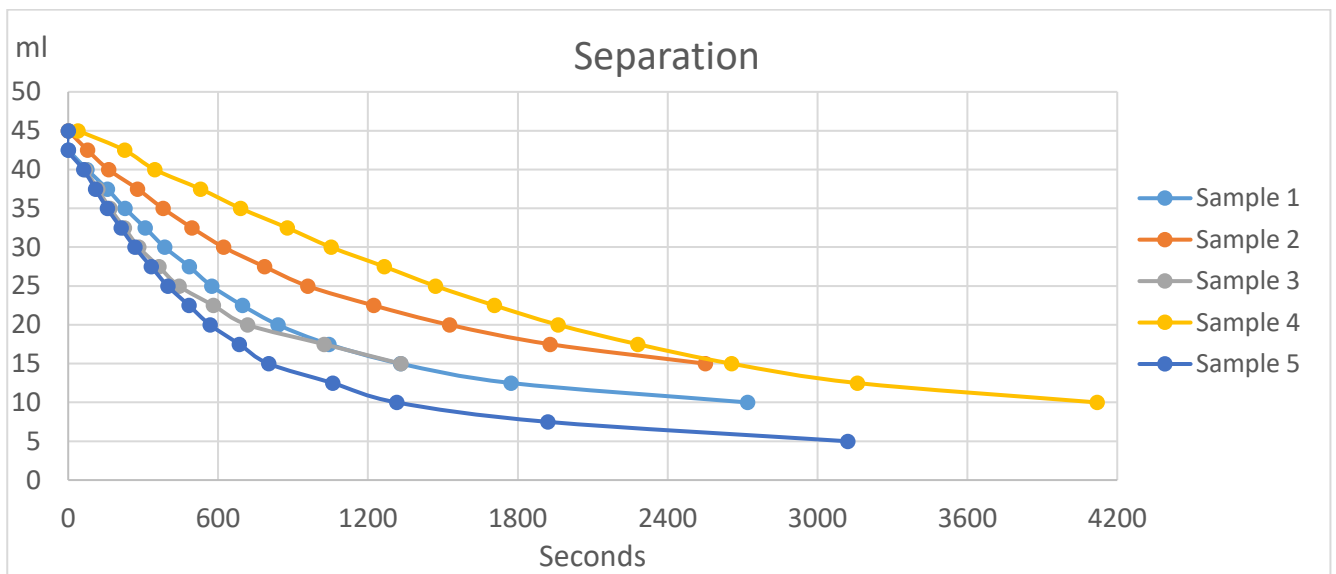
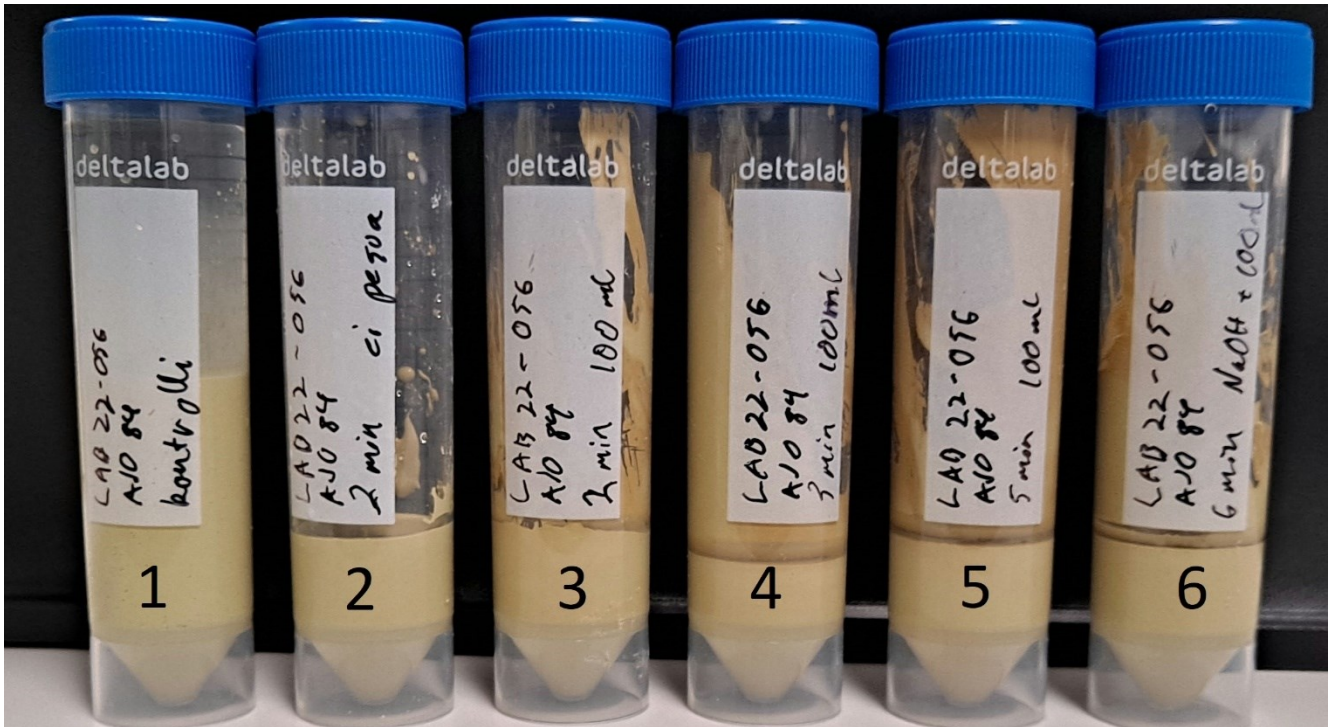


FIGURE 2. Separation time graph for five different samples. The y-axis represents the position of the solid phase's surface in the sampling tube, read from the volume measurement on the tube's side wall.

4.1.2 Filtering and washing

The problems encountered during filtering and settling could be solved by removing the liquid phase from the sample. It could be removed by filtering the sample, but filtering exposed the sample inevitably to air with the common methods like vacuum filtration, unless conducted in a protective atmosphere. Using a protective atmosphere was possible, but it was not realistic for rapid measurements outside of the controlled laboratory in a factory environment. The impact of the remaining the liquid within the sample were also unknown. Vacuum filtration with a Büchner funnel and paper filters was used for these experiments. The paper filter let through some of the smallest particles. Membrane filtration was an option, but disregarded due to longer filtering time. Retaining all particles of the solid phase was not as necessary for colour measurement as time management.

Typical sample preparation method for analyses includes thoroughly washing the sample with sodium hydroxide solution and ion exchanged water. The effect of washing on the colour of the samples was tested during the filtering tests. Washing steps also extended the filtering time and exposure to air (PICTURE 3). The longer the filtering and washing time was, the darker the sample became. An additional washing step with sodium hydroxide solution did not result in a noticeable difference compared to washing with only ion exchanged water.



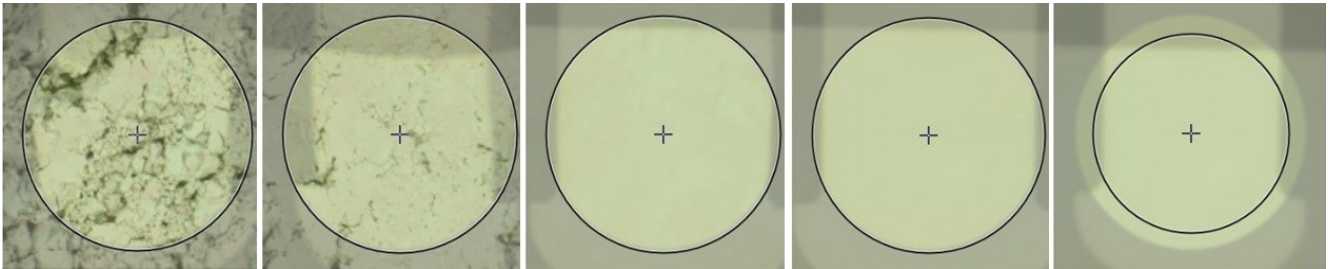
PICTURE 3. Filtered and washed samples. From left to right with the sample number in brackets: (1.) Control, (2.) 2 minutes filter time, (3) 2 minutes with 100 ml water, (4) 3 minutes with 100 ml water (5), 5 minutes with 100 ml water, and (6) 6 minutes with 100 ml NaOH solution and 100ml water.

4.1.3 Effect of moisture content on colour measurement

It was noticed that a too low moisture content caused its own issues with colour measurement. After filtering, five samples were prepared from three different experiments by adding varying amounts of ion-exchanged water to the filter cake, from none to approximately 12,5 g. The samples were mixed and analysed with the VS3200. From these analyses it was observed that too low moisture content (PICTURE 4) caused the cake to form flocks, an uneven surface and uneven colour due to shade formation. These caused unpredictable colour measurement. Too high of a moisture content caused bubbles (PICTURE 5) and separation of the liquid phase (PICTURE 2) during measurement, and an increasing error in colour measurement as the separating liquid layer grew thicker on top of the solid phase.

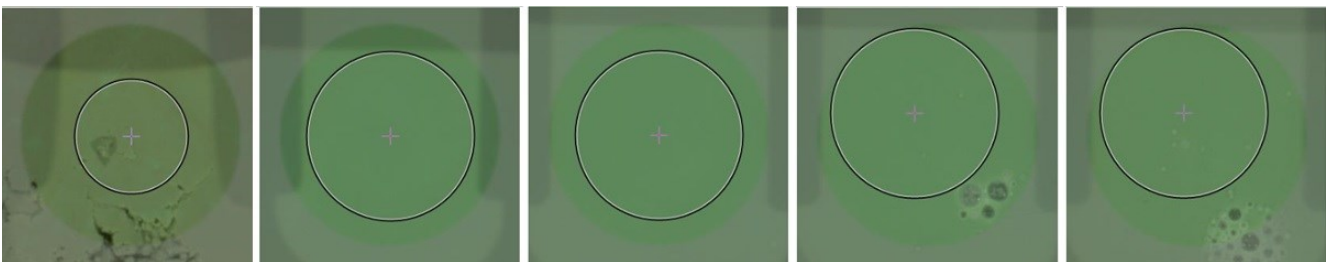
With a proper moisture content, the sample was a thick slurry with an even colour and consistency (PICTURE 1). Proper moisture content varied depending on the sample, as can be seen in the following two pictures (PICTURES 4 and 5). Ion-exchange water was added into these samples after filtering as dry as possible. In picture 4, sample with 48% total moisture by weight had a solid colour and smooth consistency while the same was achieved with a moisture content of just 28% with the sample in picture

5. Filtering quickly just until the liquid phase had disappeared around the filter cake, under thirty seconds, consistently produced a proper moisture content regardless of the sample.



PICTURE 4. Effect of moisture content, with total moisture contents ranging from left to right: 32 %, 34 %, 37 %, 43 %, 48 %. This sample displayed a particularly bad surface features at a low moisture contents.

The effect of varying moisture content was most strongly seen in the L^* and a^* values, while b^* value stayed more consistent (FIGURE 3). On the figure, green and brown lines represent the samples, and the blue line is the total moisture content, by weight, of the samples. The moisture content is displayed on the secondary y-axis. The x-axis represents the amount of added water to the sample in grams. The discoloured surface formed during filtering was scraped away before taking the samples marked as “scraped.” A coloured brown base solution was added instead of ion-exchanged water to the samples marked as “coloured.” Ion exchanged water was added to samples marked as “normal.” At low moisture contents the samples differ greatly while the results converge at middling moisture content and begin to spread out again as the moisture content increased further.



PICTURE 5. Effect of moisture content, with moisture contents ranging from left to right: 18 %, 23 %, 28 %, 34 %, 38 %. This sample displayed strong bubbling at higher moisture contents and a noticeably different colour at low moisture content.

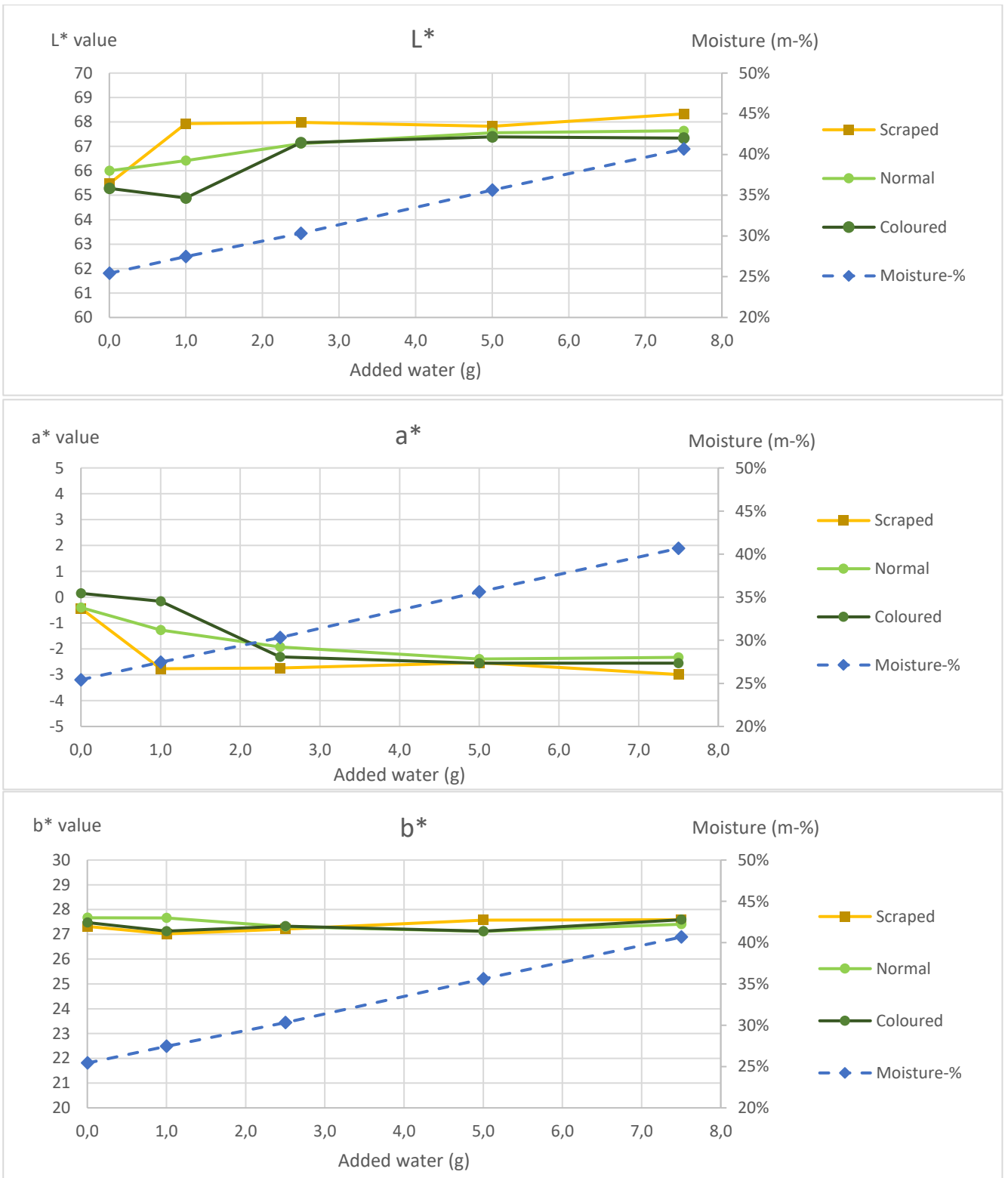


FIGURE 2. Effect of the sample's moisture content on measurements with the VS3200, charted by colour value.

4.1.4 Drying

Samples were dried in an oven leaving behind only the solid phase and the dissolved substances from the liquid phase. The dried sample would oxidize completely to a black colour either during the drying or rapidly when removed from a vacuum oven and exposed to air, which was necessary to measure colour. This was noticed when drying samples for calculating their moisture contents. Further experiments on drying the samples were abandoned.

4.1.5 Antioxidants

Some samples were treated with ascorbic acid to prevent oxidation. The acid would oxidize before the metal ions. Samples protected by ascorbic acid could not be analysed in the analytical laboratory for oxidation states as the acid disturbed the titration process, necessitating parallel samples if acid was to be used. Using an ascorbic acid produced a dramatic reduction in colour change over time with the small amounts added (0.3 g / 50 ml sample). This was first tested over a short period of time (FIGURE 4) and later with a longer period (FIGURE 5) to evaluate the complete preparation process. The consecutive measurements from the same undisturbed sample were taken automatically by the VS3200. Again, the b^* value showed less change than the L^* and a^* -values. The sample marked with red was treated with ascorbic acid and untreated sample was marked as blue. The longer experiment included three samples treated with ascorbic acid, and they were mixed after the experiment was ended and measured again. The measurement after mixing were marked on the negative time axis with square. The samples' colour returned very close to the original.

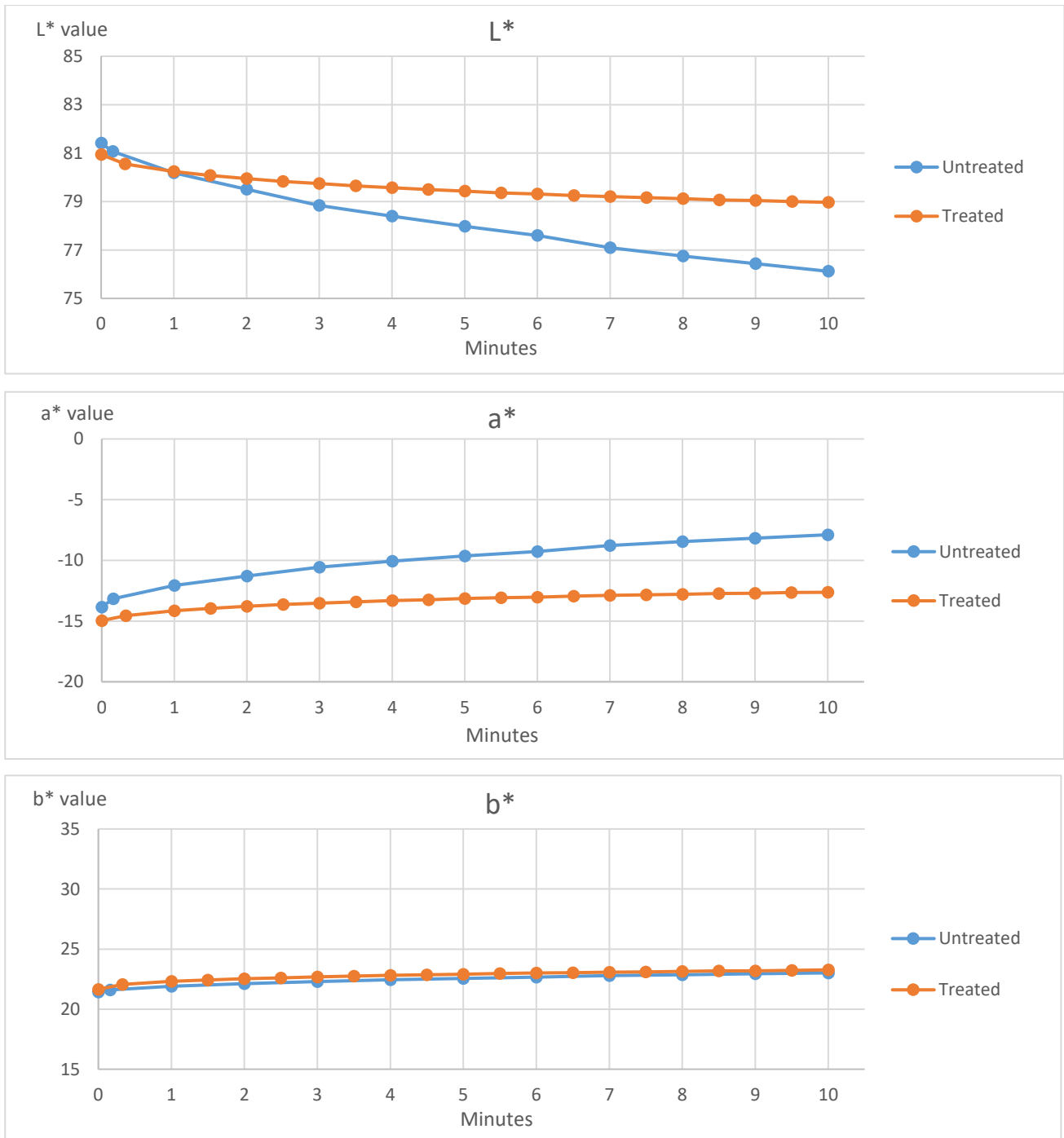


FIGURE 3. Effect of ascorbic acid on the colour change of two parallel samples over a period of ten minutes.

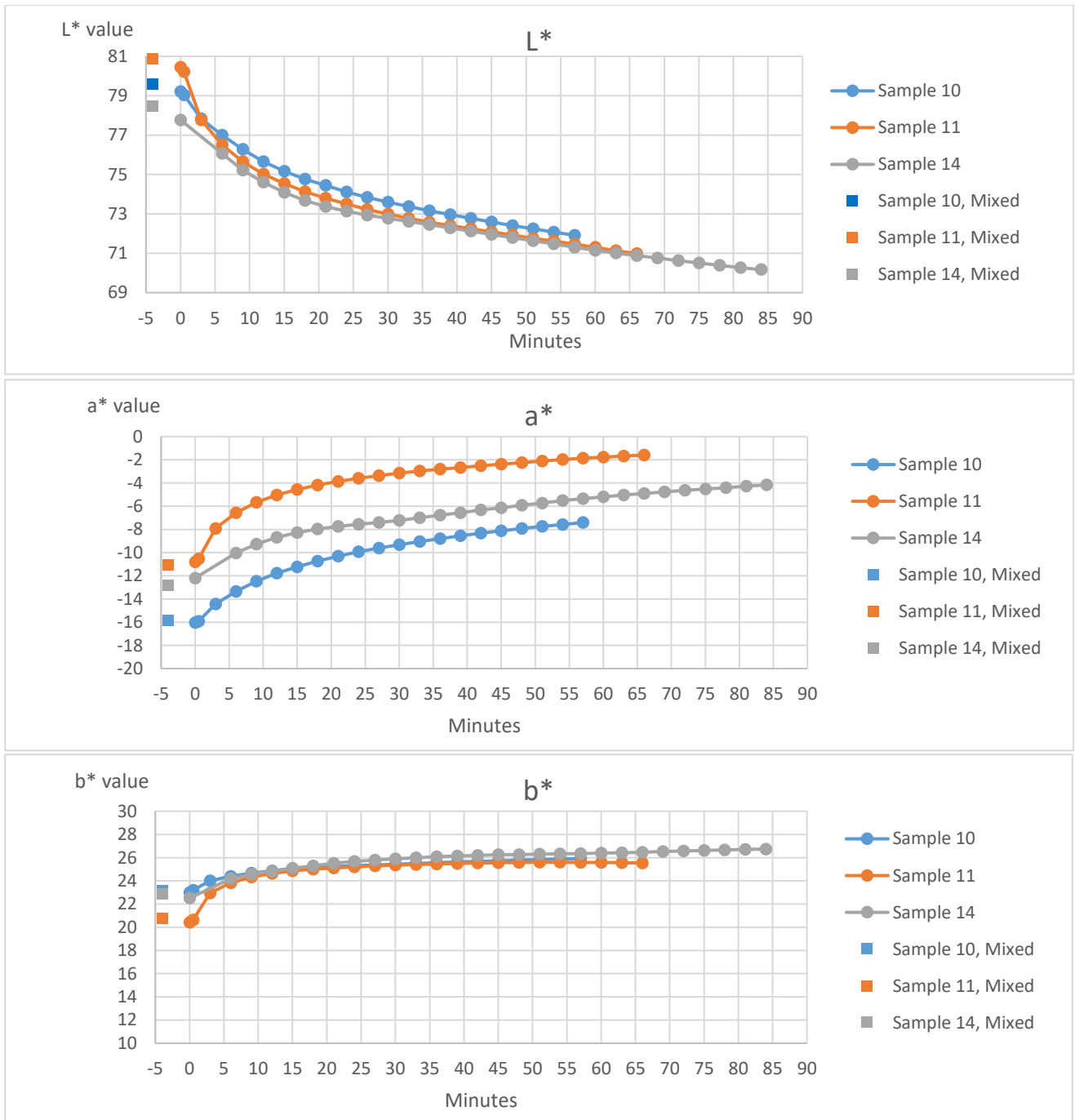


FIGURE 4. Effect of time in ambient air on the sample's colour over a longer period. Samples were mixed after the experiment and the result marked on the negative time-axis as a square.

4.2 Optimized preparation method and variables affecting colour measurement

The samples were placed into a measuring spoon and then into the VS3200, which displayed a colour analysis of the sample after a measurement time of eight to ten seconds. Some of the preparation methods were tested before the colour measurement device arrived and the personnel were trained for it. Results of these test were interpreted with a RAL K7 Classic paint colour map and by comparing control samples and samples from experiments by eye, such as in the filtering and washing experiment. These methods cannot reliably measure colour, but the differences between samples can be observed. They are subject to changing ambient light, different lighting fixtures and the individual colour vision of the person observing. Note that depending on quality of the screen or print, and individual vision, the differences in colour may not be noticeable in pictures to the reader.

Based on the results of the different experiments, a preparation method was developed: a small spoonful of approximately 0.3 g of solid ascorbic acid powder was added inside the sampling syringe before taking a sample. The sample was taken into the syringe from the manufacturing process or storage container which were kept under heavy mixing. The sample and the ascorbic acid in the syringe were mixed by hand. The sample was filtered until the liquid phase had disappeared around the edges of the cake. This took under 30 seconds and provided roughly the right consistency for colour measurement. The sampling dish was scraped full of the slurry, mixed with a small spoon to blend in the lightly oxidized surface and measured immediately with the spectrophotometer. The slurry was then mixed and measured twice more and the results averaged automatically by the VS3200. All colour measured samples were treated with this preparation method after it was chosen during the experimental phase.

4.3 Behaviour of the sample with the chosen preparation method

The second research task was to determine how the sample behaves, or oxidizes, with the chosen preparation method. Three samples were chosen and they were measured consecutively for as long as possible on the VS3200 (FIGURE 5.) The measurements were 57, 66 and 84 minutes long, with measurements being taken every three minutes after the initial ones. The measurements were stopped for other samples to be analysed or when the working day ended. The sample were thoroughly mixed in the measurement dish and measured again after the long automatic measurements. Only the very surface of the sample had changed colour and the sample returned to its original colour after mixing (FIGURE 5). It







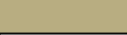


was inferred that prepared samples can be stored for at least an hour, undisturbed in ambient air. Consideration should be given to the sample drying out if left exposed for too long.

4.4 Oxidation states and correlation with colour of the sample

The third research task was to determine if there was a correlation for the colour of the sample and the oxidation states of the metals in it. The results from the experiments and colour measurement and the analysis laboratory were collected and combined. A correlation between the oxidation state ratios and colour was searched for utilizing Microsoft Office Excel.

Some samples were purposefully oxidized using oxygen gas as there was not enough variation in the samples taken fresh from the process. The 100 ml samples were placed into tall, thin measurement cylinders and the oxygen was fed to the bottom through a plastic tube. The gas rose through the sample as bubbles, mixing it constantly. The oxidized sample was divided into two. One sample was prepared and colour measured, and the other was sent to an analytical laboratory for average oxidation state measurement. The oxidized samples were prepared the same way as fresh ones with the preparation method detailed in chapter 4.2. Due to time constraints only four samples were able to be oxidized. (TABLE 3). As can be seen from Table 3, the average oxidation state of the samples barely increased despite the large colour change. The hypothesis was that only the surface of the particles was oxidized by the oxygen gas causing a large change in colour, but little change in the oxidation state.

TABLE 3. Oxidized samples with parallel unoxidized samples

Sample	Colour	Oxidized?	L*	a*	b*	Oxidation state
8.1			81,08	-9,02	17,79	2,00
8.1		X	67,12	1,96	22,06	2,13
10			80,35	-17,63	22,43	2,01
10		X	74,59	-9,46	23,69	2,03
11			78,1	-6,36	19,4	2,01
11			80,37	-10,68	20,29	2,00
11		X	70,66	-1,12	24,15	2,02
14			77,77	-12,07	22,35	2,06
14		X	66,32	-0,61	25,83	2,07

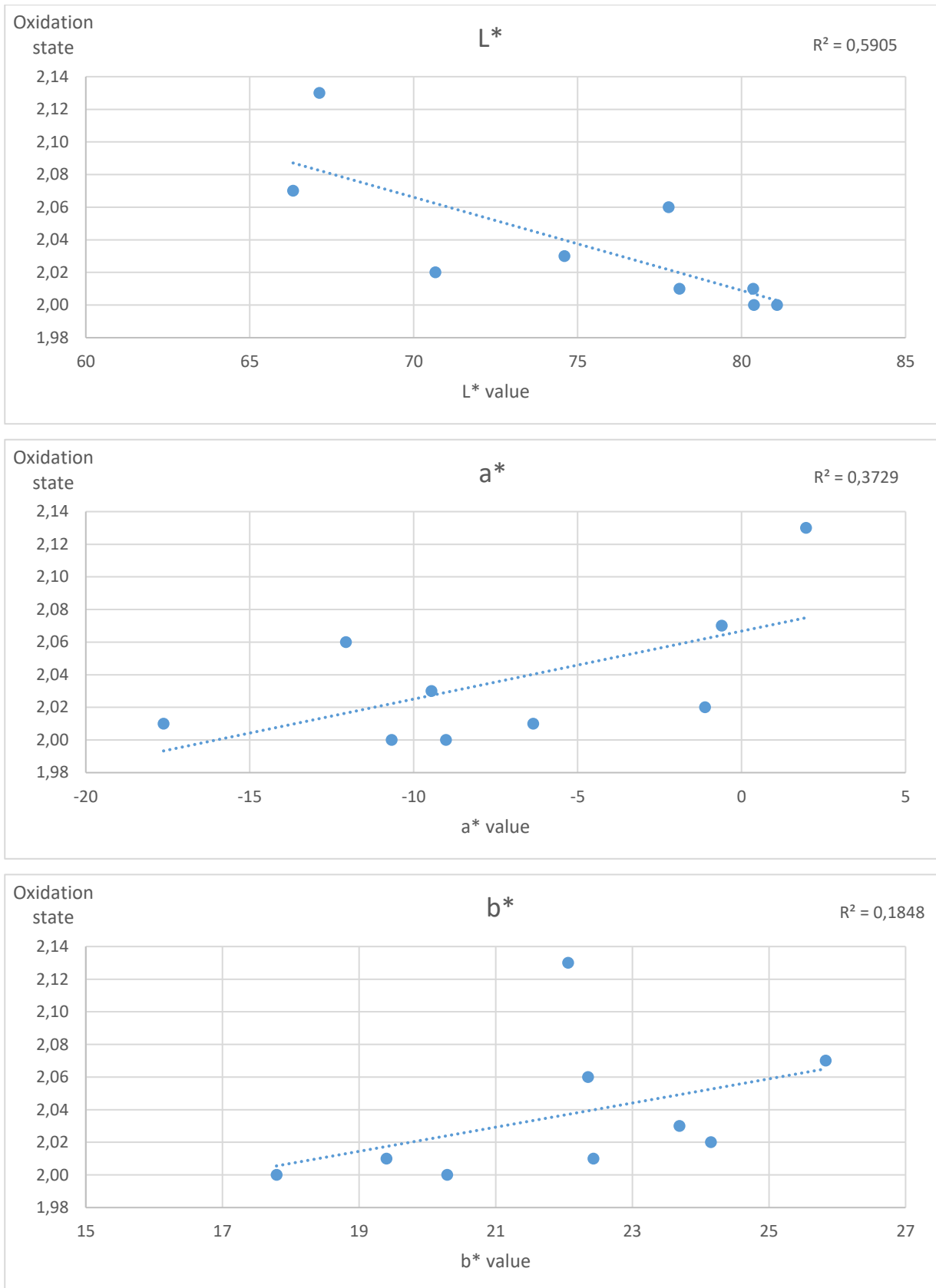


FIGURE 5. Correlation between average oxidation state and the three colour values, only samples with parallel oxidized samples are graphed.

The average oxidation state and the three colour values were plotted onto graphs from the oxidation tests (FIGURE 6) and Microsoft Excel was used to provide a trendline and R^2 -value for the three colour values. L^* , or lightness, reached the highest correlation at $R^2 = 0,6$. The two other values, a^* and b^* , reached smaller values. A significant portion of the analyzed samples had an average oxidation state of 2.00, with a range of different greens represented. The D50 particle size was fetched from laboratory results and graphed with the a^* value for measurements where it was possible. There was a moderate correlation which could be investigated further, with larger particles having a smaller a^* value, appearing greener (FIGURE 7). Similarly to figure 6, L^* and b^* did not indicate a correlation. This was in line with the conclusions of Zheng Li et al. (2020, 4–7), who highlighted powder transparency, grain size, light intensity and the solvent added as key factor influencing powder colour, with different powders acting in different ways. The grain size differences should be considered when trying to form a correlation between the average oxidation state and colour in further studies with a larger dataset.

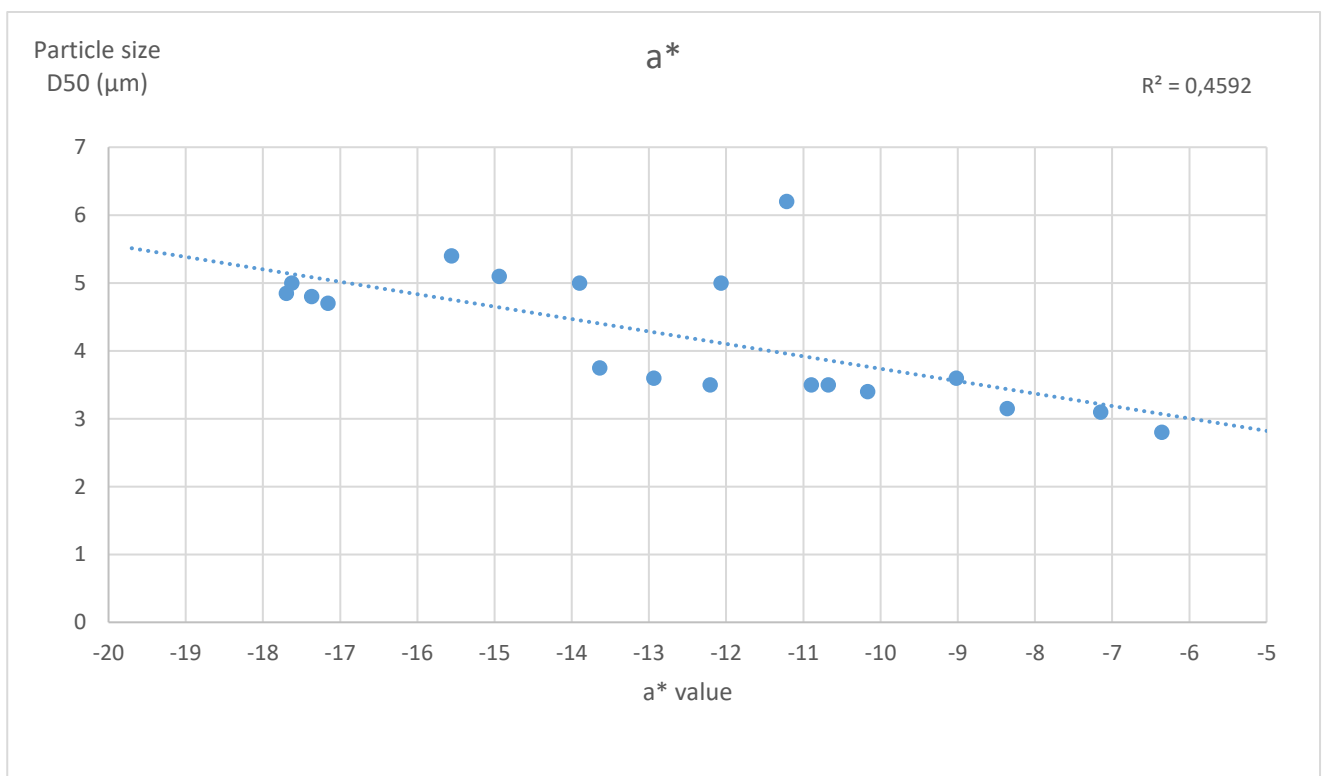


FIGURE 6. Correlation between D50 particle size and a^* -value. Negative a^* -value is greener and positive more red.

5 CONCLUSIONS

This thesis had three research tasks. The first was to find a suitable preparation method for the metal hydroxide samples. The second was to observe how the samples behaved and oxidized with the finalized preparation method. The third was to search for a correlation between the average oxidation state of the sample and the three CIELAB colour values. This thesis also functioned as a trial run for the VS3200 spectrophotometer, which was rented for a month.

The first and second research tasks were successful. A sample preparation method chosen based on empirical information and colour measurement was successful and consistent after series of experiments. The behaviour of the samples was predictable, and their rapid surface discolouration could be corrected simply by mixing the sample. (FIGURE 5.) The third task was not completely successful and a clear correlation was not found. (FIGURE 6; FIGURE 7.) The dataset was left too small due to time constraints and there were not enough samples with average oxidation states other than approximately two. While the results are not reliable enough to form a correlation with colour and the oxidation state, the possible correlation could be found with a larger dataset containing enough variation.

The results were promising, and the experiments could be continued by taking and measuring more samples. Oxidizer could also be fed into the process and not just into the samples to more thoroughly oxidize the particles. The colour measurement proved to be a fast and reliable method. The method used currently to measure average oxidation state takes hours and the samples have to be transported to another laboratory, while the colour measurement process takes about 20 minutes, including cleaning. With more measurements of a wider range of samples, a reliable correlation could be found by utilizing the relation between particle size, CIELAB colour values and oxidation state. The effect of particle size and moisture content should be considered when measuring colour, as they showed significant effect on the colour and behaviour of the samples.

This thesis was the author's first contact to professional laboratory work. The theoretical portion of the thesis proved to be challenging, as little information could be found about visible light wavelength spectrophotometry concerning opaque metals and metal compounds. The practical portion went smoothly and the author learned to work and think in a research laboratory environment professionally and conform to safety standards.

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