Optical methods for fines and filler size characterization
Evaluation and comparison

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1 Abbreviations

A  Area of particle [m$^2$]
AR  Aspect ratio of particle (length/width)
BDDJ  Britt dynamic drainage jar
BKHW  Bleached kraft hardwood
CED  Circle-equivalent diameter of particle [m]
d$_x$  Cumulative diameter of particle [m]
FT  L&W Fiber Tester
FT+  L&W Fiber Tester Plus
I  Intensity of light [W/m$^2$]
IS  ImageStream
IS$_X$  ImageStream used at 20X/40X/60X magnification
J  Bessel function
κ  Extinction coefficient (imaginary part of the complex refractive index)
k  Constant
λ  Wavelength [m]
L  Length of particle [m]
LD  Laser diffractometry
MS  Mastersizer
m  Relative complex refractive index
M  Mass of substance [kg]
n  Refractive index (real part of the complex refractive index)
$\tilde{n}$  Complex refractive index
N  Number of particles
P  Perimeter of particle [m]
PCC  Precipitated calcium carbonate
R  Radius of particle [m]
RE  Rectangle-equivalent
S  Silica
SED  Sphere-equivalent diameter of particle [m]
θ  Scattering angle [rad]
TR  Traced
TMP  Thermo-mechanical pulp
UKSW  Unbleached kraft softwood
V  Volume of particle [m$^3$]
2 Summary

The pulp fines and mineral fillers in the fine fraction of a papermaking stock influence process conditions and sheet properties. The influence is largely dependent on the size and shape of the particles. Quantitative characterization of the size and shape of fines and fillers would aid in process control and prediction of product properties. Thus, the aim of this study was to evaluate and compare optical instruments which can be used to quantitatively characterize the fine fraction of a papermaking stock. The compared instruments were the Mastersizer2000 from Malvern, based on diffraction scattering of a laser beam, the ImageStream from Amnis, and the L&W Fiber Tester and L&W Fiber Tester Plus from ABB Lorentzen & Wettre. The last three instruments are all based on imaging of the particles and have spatial resolutions ranging from 0.33 µm to about 10 µm per pixel.

All instruments overestimated the size of calibration spheres with known sizes. In several cases, calibration particles that were smaller than the spatial resolution of the instrument were detected. In these cases, the relative measurement error was large, likely due to positioning and quantization errors. It is also suggested that the oversizing was partly due to dissimilar optical properties of the calibration particles, compared to the typical sample, and that better calibration materials for fines need to be developed.

For the image-based instruments, the relative share of fines and filler particles increased as the size of the measured particles decreased. Thus, with higher spatial resolution, more particles were detected. However, the shape of the particle size distribution depended on the resolution and the field-of-view. The ImageStream resolved single PCC particles, which has not previously been done using flow microscopy. Due to its limited field-of-view, the ImageStream could not measure the largest fines, which were detected by the L&W Fiber Tester and L&W Fiber Tester Plus. While the L&W Fiber Tester Plus did not resolve single PCC particles, it detected, due to its higher resolution, a higher share of smaller particles than the L&W Fiber Tester. Overall, the ImageStream and the L&W Fiber Tester Plus were found to be complementary.

The diffraction-based method struggled to measure small fines. It is proposed that small fines diffract light insufficiently to be detected by the instrument. The obtained result was also highly sensitive to the choice of refractive index; a fact that some of the previous users apparently were not aware of.

In summary, image-based methods were found to perform better than the diffraction-based method when measuring on fines and mixtures of fines and fillers, while the highest resolution image-based instrument and the diffraction-based method were best when measuring on pure fillers.
3 Introduction

3.1 The fine fraction

This work compares the capability of different optical instruments to measure the particle size distribution of the fine fraction of a stock.

In the context of this work, the fine fraction is the fraction of a stock that passes the 76 µm opening of a Britt Dynamic Drainage Jar (BDDJ). The fine fraction may comprise up to 30% of the weight of a stock. Traditionally, the fine fraction has been synonymous with fines, i.e. the fine fraction from a pure pulp. Due to their influence on paper properties such as tensile strength, fines have attracted increased interest from the industry. This has led to demands of new methods for their characterization.

Paper is rarely made of pulp alone, but also contains mineral fillers and other additives. Additionally, a stock may comprise recycled pulp or broke. Then, the fine fraction may contain fines, mineral fillers/pigments, latex fragments, starch, and agglomerates of the above mentioned particles. In summary, the fine fraction is a heterogeneous collection of particles of different sizes, shapes, and material composition. Rod-shaped fibrillar fines may have widths from 20 nm (nanofibrils) to several micrometers (macrofibrils) (Chinga-Carrasco 2011). Rectangular flaky fines and ray cells have lengths and widths of tens of micrometers (Rodrigues Alves 2011). Fillers may have plate-like or spheroid shapes, and are often sized around 0.5 µm (LUT 2012). The heterogeneity and polydispersity puts high demands on instruments used to analyse the fine fraction. The instrument should be able to measure both the smallest and largest particles, and to distinguish different shapes.

It is rarely possible to differentiate between different material types in the fine fraction. Thus, it would be convenient to be able to characterize a mixed suspension of e.g. fines and fillers. Currently, no commercial measurement system is advertised for this task. However, developments in particle measurement technology make it worthwhile to evaluate if commercially available systems may be used.

3.2 Measurement techniques and evaluation

3.2.1 Particle characterization

Measurement instruments for microparticle characterization have been developed for many application areas. Optical methods have the advantage of being non-destructive and fairly easy to automate, but have a limited spatial resolution. Optical methods that have been used to measure on fine fractions include light microscopy, flow microscopy, laser diffractometry, flow cytometry, depolarizers, FBRM, and turbidity-based instruments. A review of the subject was made by Hyll (2015).

It is often unclear how a measurement instrument performs for particles with sizes close to the spatial resolution of the instrument. For example, the resolution of the instruments is often evaluated using particles with shape and composition dissimilar from fines. The particles used in the evaluation tend to have optical properties that make them much easier to detect than fines. Thus, when measuring on fines, it is not given that the instrument performs according to specifications. To verify the instrument performance for fines, calibration particles with properties similar to fines must be used.
The following section will focus on the techniques utilized in this work. First, the principles of flow microscopy and laser diffractometry are presented. Necessary considerations when comparing between different measurement methods are then discussed. Previous studies comparing the techniques are summarized. Finally, aspects of the validation of measurement instruments are discussed.

### 3.2.2 Flow microscopy (dynamic image analysis)

In flow microscopy, a stream of particles pass through a flow cell illuminated with a light beam. The transmitted light is then captured by a CCD detector, forming an image (see Figure 3.1). The contrast in the image is due to particles absorbing or refracting the light, or scattering it in directions other than the direction of the incident beam. Since it is the transmitted light that is measured, opaque particles will be darker, while transparent particles will be brighter. Compared to static microscopy, where the particles are fixed onto a glass plate, flow microscopy has the advantage of measuring many particles during a short period of time; thus providing quantitative statistics. However, partly due to the unrestricted movement of the particles, the resolution of flow microscopes becomes limited, compared to the higher resolution of static microscopes.

![Flow microscope diagram](based on PSS 2015)

**Figure 3.1.** Principle of a flow microscope (based on PSS 2015).

Fibre analysers using flow microscopy as their measurement principle have been used in the pulp and paper industry since the 1980’s. Today, a wide range of analysers are available, for example the FiberLab (Metso Automation), the Morfi (Techpap), the PulpEye (PulpEye), the Fiber Quality Analyser (FQA, OpTest), and the L&W Fiber Tester (Lorentzen & Wettre). The majority of these instruments are mainly adapted to measurements on fibres and, to some extent, vessel and ray cells. Morphological studies on fines have been made with some prototype setups with higher spatial resolution (e.g. Luukko 1999; Krogerus et al. 2002; Kangas and Kleen 2004) and with flow
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microscopes developed for other application areas (Ferreira et al. 1999; Mörseburg 1999).

In fibre analysers, the typical output is the length-weighted length $L$ and width $W$ of fibres. According to ISO-standards, fibres are defined as the particles in the pulp that are longer than 200 µm (ISO 16065-2). Often, additional criteria are added, for example that the aspect ratio (length/width) must be above 4. According to ISO-standard, at least 5000 fibres should be measured to provide sufficient statistics. Most fibre analysers also count particles smaller than 200 µm (but large enough to be detected by the instrument), and classify them as fines. However, while a count of fines (fines content) is provided, size and shape data on the fines has traditionally not been given. Additionally, the flow microscopes have not been designed for analysis of fillers or fines-filler mixtures. This depends on several factors:

- **Image resolution**
  - Typically around 10 µm/pixel. That is not enough to detect a large share of the fines, or the majority of fillers.

- **Image contrast**
  - Fines have optical properties (refractive index) similar to water, making them faint and difficult to distinguish from the image background (water) even if the spatial resolution is sufficient.

- **Particle segmentation**
  - Algorithms for segmenting a particle from the image background are adapted to the size, shape and optical properties of fibres, and not for fines or fillers.

- **Size and shape criteria**
  - Image analysis criteria created to remove noise, air bubbles and debris may unwantedly remove fines and fillers. For example, that a particle should be $\geq 2$ pixels in size, and not round.

- **Analysis geometry**
  - When length and width are calculated, the particles are often assumed to be elongated and rectangular. For fillers in particular, that assumption may result in errors.

Instruments have handled the limitations by focusing on a narrow size range, having two cameras with different resolutions, and/or having several flow cells or magnifications. Only recently, improvements in camera technology have allowed single cameras to detect smaller particles while retaining the ability to measure large particles. However, the spatial resolution of these wide range instruments is still an order of magnitude lower than the typical size of fillers. When measuring on the fine fraction, it is not necessary to be able to characterize large particles (e.g. fibres). Thus, flow microscopes focused on smaller particles are also of interest, as are other optical techniques with resolutions that allow for the detection of fillers.

3.2.3 Laser diffractometry (static light scattering)

Laser diffractometry is marketed with a wide measurement range; from 20 nm to over 3000 µm. Thus, it has the potential to be suitable for analysing the polydisperse fine fraction. In laser diffractometry a collection of flowing particles is illuminated by one or
more laser beams, see Figure 3.2. The beam is scattered by the particles at different angles dependent on the size of the particles. The spatial scatter distribution, primarily caused by diffraction, is then collected by a range of detectors, and converted to a particle size distribution by solving the inverse scattering problem (Bodycomb 2012). Some instruments also utilize the polarizability of the light in order to improve the detection of small particles.

![Figure 3.2. Principle of laser diffractometry (based on Malvern Instruments 2005a). The size range of a typical instrument is around 0.02-3000 µm.](image)

Most instruments use the Mie theory to relate the measured spatial scatter distribution to the particle size. The theory was developed for spherical particles of any size, provided that they are packed sparsely enough to act as independent scatterers. Since the Mie equations are complex to solve, simpler approximations are used whenever possible. For example, the Rayleigh approximation may be used when the particles are small compared to the wavelength of the light, and the Fraunhofer approximation may be used if the particles are opaque and large compared to the wavelength. When measuring on a fine fraction, it will generally be necessary to use the Mie theory, as a wide range of particle sizes is present.

If a coarse approximation of the Mie theory is made, the spatial scatter distribution is given by:

$$I_\lambda(\theta,R,m) = I_0 \left( \frac{k^4 R^6 (m - 1)^2 \theta^6}{8\pi^2} + (K_1 \theta) + (K_2 \theta)^3 + (K_3 \theta)^5 + k^2 R^4 J_1^2 \theta^{-1} \right) \quad [\text{Eq. 1.1}]$$

where $I_0$ [W/m²] is the intensity of the illuminating monochromatic beam, $k$ [m⁻¹] is the wave number $(2\pi / \lambda)$, $K$ are constants, $R$ [m] is the radius of the particle, $J_1$ is the 1st order Bessel function of the first kind, $\theta$ [rad] is the angle of the scattered light, and $m$ is the relative complex refractive index (Keck and Müller 2008).

The first term in the equation is the Rayleigh-term, which dominates when the particles are small relative to the wavelength. Here, the scattering is proportional to $R^6$ and $m$. Thus, the intensity drops quickly with decreased size and increased wavelength. The last term is the Fraunhofer-term, which dominates when the particles are large. Here, the scattering is dependent on $R^4$, but not dependent on $m$. Larger particles will scatter light...
more intensely than smaller particles, and the scattering will mainly be of the diffraction type; in the forward direction of the beam.

If the goal is to solve the equation for the particle size, the other unknown parameter, the relative complex refractive index \( m \), must be provided to the instrument software. The relative complex refractive index is the ratio of the complex refractive index \( \tilde{n} \) of the sample to that of the surroundings:

\[
\begin{align*}
  m &= \frac{\tilde{n}_{\text{sample}}}{\tilde{n}_{\text{surroundings}}} \\
  \tilde{n} &= n + i\kappa
\end{align*}
\]

[Eq. 1.2]

where the real part \( n \) is simply called the refractive index, and the imaginary part \( \kappa \) is called the extinction coefficient. Both may be dependent on wavelength, temperature, and other factors. Often, data on the extinction coefficient is lacking in the literature.

Since Mie theory was developed for spherical particles, all particles are assumed to be spheres, and the output is expressed as sphere-equivalent diameters (SED), see Figure 3.3. Consequently, it is not possible to infer particle shape from laser diffractometry data. Another common output is cumulative diameters, \( d_X \), which is the diameter at which a certain percentage of the sample has sizes below that diameter. For example, 10% of a sample would have sizes below the \( d_{10} \) diameter.

**Figure 3.3.** The concept of sphere-equivalent diameter (SED).

Laser diffractometry has been used in many studies to characterize fines and fillers (Hyll 2015). At least two studies have used laser diffractometry to characterize mixtures of fines and fillers (Hirsch 2012; Baosupee et al. 2014). Regrettably, the assumed refractive index was only stated in a single work: Xu and Pelton (2005) used a refractive index of 1.53 for fines, with no motivation given.

### 3.2.4 Comparing data from different instruments

As laser diffractometry does not give morphological information, the results can be difficult to interpret. By comparing with results from imaging measurements, where the particles can also be visually inspected, the results may be better understood. When comparing data from different instruments, it is necessary that: (1) the weighting is the same, and (2) the compared parameter (e.g. area, length) is the same.

Image-based techniques give inherently number-weighted data, which can easily be transformed to length-, width-, or area-weighted (Horiba 2012). To do volume-weighting, the geometry (shape) of the third dimension of the particle must be known or assumed, as imaging only provides the projected (2D) geometry. Laser diffractometry gives inherently volume-weighted data. Transforming from volume-weighted to number-weighting is perilous, as no information of the shape of the particle is available (Horiba 2012). Thus, when comparing between imaging techniques and laser
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diffractometry, it is advisable to transform the image-based data to volume-weighted, rather than transforming the laser diffractometry data to number-weighted.

To assure that the compared parameter is the same, one needs knowledge of how an instrument calculated the obtained value. The length of a particle – usually defined as its longest extension - can be calculated in a number of different ways. A traced length will not be the same as a rectangle-equivalent length, see Figure 3.4. Even if it is known how the parameter is calculated, differences in how the binarized particle is segmented from the greyscale image may result in significant measurement differences.

Figure 3.4. Example of geometries and parameters for image-based particle size characterization.

As laser diffractometry only provides a single output parameter; the sphere-equivalent diameter, a comparison between this technique and imaging requires that a similar, single parameter is calculated from the imaging data. The contributed diffraction from a single particle is often said to be proportional to its random projected area (Kelly and Kazanjian 2006). Thus, circle-equivalent diameter (CED) is often the imaging parameter used in comparisons. However, it is rarely clear if the proportionality to the random projected area refers to data obtained using the Fraunhofer approximation, or data obtained using the Mie theory. In a study on rectangular particles where the Fraunhofer approximation appears to have been used, it was found that a sum of length- and width-weighted area gave a better correlation with laser diffractometry data than the CED (Tinke et al. 2006).

While laser diffractometry was used in many studies on fines, only a single study was found where both quantitative imaging and laser diffractometry data were reported for the same sample (Ferreira et al. 1999). Only mean values were reported, and it was found that the volume-weighted mean SED obtained by laser diffractometry was larger than the number-weighted mean longest linear dimension obtained by static microscopy and flow microscopy.

3.2.5 Validating measurement instruments

Calibration particles

Calibration particles are used to test measurement instruments against the specification provided by the manufacturer. Calibration particles should have similar size, shape, and optical properties as the particles that are normally measured.

For fibre analysers, rayon fibres have traditionally been used as calibration material. Rayon fibres can be manufactured to well-defined sizes and have suitable aspect ratios,
but they are much larger and not suitable as calibration particles for fines. Nanocrystalline cellulose (NCC) can also be manufactured to well-defined sizes, but is smaller than the resolution of most optical analysers. Additionally, NCC particles usually have a much lower aspect ratio than the typical fibril.

The ideal calibration particles for fines are rod-shaped and micron-sized. While such particles have been evaluated, they are not commercially available (Kelly and Kazanjian 2006). Currently, NIST researchers carry out non-commercial production of rod-shaped particles wider than 5 µm and longer than 30 µm, in an epoxy material with refractive index 1.61 (Ripple et al. 2013). It has proven difficult to find manufacturing methods for materials with optical properties similar to that of organic samples, which tend to have refractive index around 1.40 (Carrier 2014).

With a refractive index around 1.59, polystyrene microspheres may constitute suitable calibration material for fillers. In flow cytometry, silica microspheres are starting to replace polystyrene microspheres, as the refractive index of silica (1.41-1.43) is much closer to that of the organic samples that are normally analysed (Foladori et al. 2008; Totoki et al. 2015). In terms of optical properties, silica microspheres are similar to wet fibres; which has an estimated refractive index of 1.41 (chemical pulp, Kienle et al. 2008) or 1.42 (mechanical pulp, Wood and Karnis 1996).

In summary, there is a lack of calibration particles for the evaluation of instruments suited for fines measurements. Silica microspheres may be the best option in terms of optical properties. However, the shape is not ideal.

Sources of uncertainty

All instruments possess uncertainty in the measurement result. The total uncertainty is a sum of the uncertainties from sampling, sample dispersion, internal and external noise, temperature fluctuations, particle orientation, air bubbles, carryover (particles lingering in the system from previous measurements), segmentation algorithm (for image-based methods) or mathematical model (laser diffractometry), and many other factors. Most automated instruments begin the measurement process by measuring on pure water. The procedure allows the system to correct for several of the factors above.

To estimate the other contributions to the measurement uncertainty, a common validation procedure is to do measurements on particles of well-known size and shape. The relative error in accuracy for the measured quantity $X$ can then be calculated as a percentage:

$$\text{Error} = 100 \times \left| \frac{X_{\text{measured}} - X_{\text{reference}}}{X_{\text{reference}}} \right|$$  \hspace{1cm} [Eq. 1.3]

For a monodisperse sample, the mean can be said to be the best approximation of the true size of the particles, and the standard deviation of the mean reflects the uncertainty of the measurement. For polydisperse samples like pulp, there is no single “true” size which the mean can approximate, and the standard deviation of the mean is thus of little meaning. However, the reproducibility of the measurement can still be estimated by calculating the mean and standard deviation of several independent samples (different
samplings from the sample source). International standards recommend at least three independent samples. In practice, two independent samples are common.

Standard deviation is not provided by most laser diffractometers. Instead, the span is often provided as an estimate of the distribution width:

\[
\text{Span} = \frac{d_{90} - d_{10}}{d_{50}}
\]  
[Eq. 1.4]

where \(d_X\) is the cumulative diameter, and \(X\) is 10\%, 50\%, or 90\%, respectively.

Image-based instruments have some additional sources of uncertainty. If a particle is not imaged on the centre of a pixel, but instead on the vertex between several pixels, its light will be spread out and a positioning error may be introduced (Brown 2009). During the thresholding of the intensity values of the original greyscale image, which is necessary to differentiate the particle from the background, a quantization error may also be introduced. If the threshold is high, fainter parts of the particle may be classified as background, and the particle size becomes underestimated. If the threshold is low, the particle size may be overestimated. The magnitude of the positioning and quantization errors increases with decreasing particle size relative to the pixel size. However, these errors may be difficult to separate from other measurement errors.

3.3 Aim of study

Based on this background, the aim of the study was threefold. As a share of the fine fraction is very small in size, the spatial resolution of the measurement instrument is of great importance. However, the performance of the instruments has not been evaluated with calibration particles with optical properties similar to fines, and sizes close to the resolution of the instruments. The first objective of the study was to investigate instrument performance at the resolution limit using calibrated “fines mimicking” particles.

Few studies have been made where flow microscopy was used to measure the morphology of fines, and no studies were found on pure fillers, or a mixture of fillers and fines. Recent developments have increased the spatial resolution of flow microscopes. Thus, the second objective of the study was to evaluate the performance of flow microscopes when measuring on pure fines, pure fillers, and a mixture of fines and fillers.

Studies on fines, fillers, and mixtures of them have been done using laser diffractometry, but the results have been difficult to interpret. The third objective was therefore to investigate if the morphological information from the imaging instruments could be used to improve the interpretation of the laser diffractometry results.
4 Materials and methods

4.1 Measurement instruments

The main properties of the instruments compared in this work are summarized in Table 4.1. Detailed information about the respective instrument is provided in the following sections.

<table>
<thead>
<tr>
<th></th>
<th>MS</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
<th>FT+</th>
<th>FT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resolution [per pixel]</td>
<td>~ 20 nm</td>
<td>0.33 µm</td>
<td>0.5 µm</td>
<td>1.0 µm</td>
<td>~ 4 µm</td>
<td>~ 10 µm</td>
</tr>
<tr>
<td>Field-of-view or maximum size</td>
<td>2000 µm</td>
<td>40 µm x 170 µm</td>
<td>60 µm x 256 µm</td>
<td>120 µm x 512 µm</td>
<td>~ 10 000 µm x 8 000 µm</td>
<td>~ 13 000 µm x 10 000 µm</td>
</tr>
<tr>
<td>Raw data weighting</td>
<td>Volume</td>
<td>Number</td>
<td>Number</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Used output</td>
<td>SED</td>
<td>Length, width, area, perimeter</td>
<td>Length, Width</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Measurement time</td>
<td>10 minutes</td>
<td>3 minutes*</td>
<td>10-20 minutes</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Sample volume</td>
<td>20 or 60 ml</td>
<td>0.2 ml</td>
<td>200 ml</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1. Main properties of the compared measurement instruments (Malvern Instruments 2005b; Amnis 2012; Grahn and Björk 2013; L&W 2014). **MS**: Mastersizer. **IS_X**: ImageStream using 20X/40X/60X magnification objective. **FT+**: L&W Fiber Tester Plus. **FT**: L&W Fiber Tester. *Excluding analysis.

4.1.1 Mastersizer2000

A Mastersizer 2000 (www.malvern.com) was used for the laser diffractometry measurements. A photo of the instrument and its flow cell is shown in Figure 4.1.

![Figure 4.1. The Mastersizer2000 from Malvern. The flow cell can be seen as the round window in the centre of the image.](image)

The instrument utilizes two lasers to produce the scattering pattern; a blue 466 nm laser and a red 633 nm laser. The shorter wavelength of the blue laser extends the detection range to smaller particle sizes. 52 detectors are placed at different angles around the flow cell to measure the forward-, side-, and back-scattered light.

During the measurement procedure, the background was first measured with only water in the sample dispersion unit, using automated routines. A few drops of sample were dripped into the sample dispersion unit, which was equipped with a propeller stirrer.
The light extinction level was monitored, and sample or water was added until the light obscuration was within a certain threshold. Three data collections were made on the same sample, and the results were averaged. Two independent measurements were made on the same sample, and the final results presented as the average of all six data collections. Between each sample, the dispersion unit was cleaned with water.

The analysis software supplied with the instrument was used to extract the data. At this stage, the complex refractive index was set according to the values given in Sections 4.2.2 and 4.2.3. Only a single refractive index could be set for each sample type. However, for some samples, a range of refractive indices above and below the ones given in Sections 4.2.2 and 4.2.3 was evaluated, in order to study the sensitivity of the results.

The software calculated the volume-weighted percentage on a user-defined logarithmic x-axis. As no particles with SED larger than 1000 µm were seen, an x-axis ranging from 0.020-1000 µm was used, with 50 logarithmically spaced data points. The volume-weighted mean value, and $d_{10}$, $d_{50}$, and $d_{90}$ cumulative diameters were also exported.

Advanced options for restricting the maximum and minimum particle size and for using other weightings than volume-weighting were available. Surface area-, length-, and number-weighting of the inherently volume-weighted data could be performed. While using other weightings was not recommended due to an associated increase in uncertainty, the other weightings were evaluated for a single sample in order to study the impact on the particle size distribution.

4.1.2 L&W Fiber Tester and L&W Fiber Tester Plus

The L&W Fiber Tester (“FT”) and L&W Fiber Tester Plus (“FT+”) instruments from ABB Lorentzen & Wettre (www.l-w.com) are flow microscopes developed for pulp analysis. The FT+, which is shown in Figure 4.2, has a higher resolution than the FT, and more algorithms adapted for fines analysis. As a value of the spatial resolution of the FT+ was not available, a value of approximately 4 µm was calculated based on saved greyscale images from measurements of silica spheres with known size.

In both instruments, the sample is automatically diluted to suitable concentration. The particle stream is put through a flat, rectangular flow cell and several particles are imaged at the same time. In an automated procedure, half of the volume of the diluted sample is first measured, and the results are compared to those from the second half of the sample. This verifies the reproducibility of the measurements.

The obtained greyscale images are background corrected and then binarized into black-and-white images using a certain intensity threshold. The particles are then segmented based on certain assumptions on size and shape.
In the standard settings of the FT, the smallest particles reported are 40 µm in length and 40 µm in width, i.e. about 4 pixels in size (L&W 2010). In the default settings, if the particle is longer than 200 µm, has an aspect ratio over 4, is at least five pixels big, and not wider than 75 µm, it is classified as a fibre. Particles with aspect ratio less than 4 are classified as round objects. The fibre must not be curled so much that it crosses itself, which is reflected in the criteria that the parameter called the “shape” must be larger than 50%. Particles shorter than 100 µm or 200 µm are, dependent on the standard used, classified as fines. Particles that are 2 to 5 pixels in size are classified as “five-pixel” objects, which can be included in or excluded from the data. The FT+ uses the same fibre criterion as the FT except for the minimum number of pixels needed, which is not used in the FT+. The definition of fines is the same as for the FT.

The base parameters calculated by the FT/FT+ are the area $A$ and perimeter $P$ of the particle (Karlsson and Fransson 1997; Karlsson 2006; Fransson and Schärman 2015). The length and $L$ the width $W$ are assumed to be equal to those of a rectangle with the same area and perimeter as the measured particle.

$$\begin{align*}
A &= LW \\
P &= 2W + 2L
\end{align*}$$

[Eq. 1.5]

The length and width are obtained by solving the equation system given by the above equation (Fransson and Schärman 2015). A calibration offset is then added to the width (Ström 2015):

$$\begin{align*}
L_{RE} &= \frac{P}{4} + \frac{\sqrt{P^2/16 - A}}{2} \\
W_{RE} &= \frac{P}{4} + \frac{\sqrt{P^2/16 - A} + \text{offset}}{2}
\end{align*}$$

[Eq. 1.6]

where the subscript $RE$ stands for rectangle-equivalent. For low aspect ratios, the offset may result in a width that is larger than the length. To calculate the shape $S \%$, also called the shape factor or shape ratio, the projected length $L_P$ of the fibre (close to the distance between the fibre ends) is divided by the rectangle-equivalent length:

$$S = \frac{L_P}{L_{RE}}$$

[Eq. 1.7]

In the measurement procedure, the instrument settings were changed so that (1) individual data values for particles shorter than 200 µm (fines) were included in the raw data, (2) the fibre criteria was disabled (the aspect ratio was allowed to be lower than four), (3) objects smaller than 2 pixels in size were not removed, and (4) round objects were not removed. The FT was set to measure on 60 000 fibres, or until 20 minutes had passed, while the FT+ was set to measure on 100 000 particles, or until 20 minutes had passed. Two independent samples á 200 ml were measured on each fine fraction.

The raw data with values for each particle was exported, comprising number-weighted rectangle-equivalent length, width and shape ratio. The smallest particle appearing in
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the data had a length of 15 μm for the FT, and 4.0 μm for the FT+. The shape was not used as its calculation was not adapted for small particles. The FT+ provided two additional parameters; the fibril perimeter and the fibril area. These values are calculated on bound fibrils (i.e. fibrils that are still attached to the fibres). Since this work used fines only, the fibres had been screened away, and the additional parameters were not used.

In one of the measurements, greyscale images were saved for visual inspection. A few examples of particles found in the images are shown in Figure 4.3. Regrettably, there is no easy way to locate the particle in an image from which a specific length and width is measured. Thus, the exact measured dimensions of the particles in Figure 4.3 could not be obtained.

Figure 4.3. Zoomed-in Fiber Tester Plus greyscale images of a mixture of unbleached chemical SW and PCC.

4.1.3 ImageStream® Mark II
The ImageStream® MarkII (http://www.merckmillipore.com/) is an imaging flow cytometer (see Figure 4.4). Instead of a traditional flow cell, the ImageStream uses hydrodynamic focusing. In hydrodynamic focusing, a sheath fluid encompasses the sample fluid and focuses it into a thin, laminar stream. Ideally, the hydrodynamic focusing lets only a single particle be illuminated in each image. In practice, a share of the images will contain multiple particles, making those images unusable or difficult to interpret. This occurs especially if the particle concentration of the sample is high.

Figure 4.4. Left: The ImageStream instrument. Right: The flow cell and microscope objectives of the ImageStream
As the fluid channels of the instruments are narrow, screening the sample through a Ø75 µm mesh prior to measurement is advised (Amnis 2013). When measuring on a fine fraction, this condition is already fulfilled due to the BDDJ screening.

The ImageStream system used in this study had three microscope objectives, each providing a different resolution and field-of-view, see Table 4.1. In addition to brightfield illumination for the microscopy image, the system was equipped with a 488 nm laser for fluorescent excitation and a 785 nm laser for side-scattering measurements. However, in this work, it was only used as a high-resolution flow microscope.

The transmitted, emitted (fluorescent), and side-scattered light from the illuminated particle is split into several wavelength ranges and projected onto a CCD. The synchronization between the CCD and the particle flow is made by high-scattering polystyrene spheres that are always running in the particle stream. These “SpeedBead” particles can be separated from sample particles based on their well-defined size and scattering properties.

The images are processed to remove background noise and transferred to the associated analysis software (IDEAS) in grey scale format, see Figure 4.5. Images containing particles that are long enough to nudge the edges of the field-of-view (see Table 4.1) are automatically discarded. Thus, fibres flexible enough to pass the screening would not be seen in the ImageStream. However, they would be seen in the FT+, as its field-of-view is much larger. Thus, while the FT+ is adapted to study also bound fibrillary (fines), the ImageStream is only capable of measuring free fines.

![Figure 4.5. Example of an ImageStream image. A beam splitter splits the signal into several wavelength ranges (“channels”) : each giving one image.](image)

In the analysis software, the user may choose between several algorithms to segment the particles from the background. Parameters such as area, traced length, or intensity in different channels can then be obtained from the segmented images.

By plotting parameters against each other in a scatterplot, particle types of interest are identified. The population can be separately evaluated by enclosing it with a boundary
region, see Figure 4.6. Analysis by scatterplots and regions is a standard procedure in flow cytometry.

Figure 4.6. Scatterplot of particle area vs. side-scattering intensity for a sample of 2 µm silica spheres. Left: Density plot, where a red colour represents a higher relative occurrence. Images associated with different populations have been added for illustrative purposes. Right: Plot with regions around the denser populations.

For the measurements in this work, 100 µl of sample was put into the sample tube. The settings were to measure 10 000 particles, provided that they were in-focus (as determined by their Root-Mean-Square intensity) and not SpeedBead particles. The samples containing PCC were measured without SpeedBead particles, as the optical properties of PCC were similar enough to allow them to track the flow. Five independent measurements were made on each sample. The data was then processed in the IDEAS analysis software supplied with the instrument.

The aim of the IDEAS analysis was to obtain the subset of particles containing single particles in focus. Based on previous experience, the “Sample” segmentation algorithm was used (see Figure 4.7), as it was known to work well on fines and decently on other particles. For large PCC particles, diffraction of light creates a bright halo around the particle, causing the algorithm to overestimate its size. The “Sample” segmentation algorithm was based on a combination of skeleton, erosion and active contour image processing algorithms. As erosion was used, features (noise or particles) that were only a single pixel in size were removed.
Figure 4.7. Segmentation result (blue area) for different segmentation algorithms.

Particles with a combination of small area and weak gradient, making them difficult to distinguish from noise, were removed. To estimate the influence of this step, particle size distributions with and without the removed particles were compared. No significant difference was observed. Images containing multiple particles were also removed, based on the spot count and total side scattering intensity in the image, see Figure 4.6. A general impression was that the IS20X data was much more difficult to analyse than the IS40X and IS60X data, due to its coarser resolution.

Finally, once the population with “single particles in focus” was identified, the area, perimeter, traced length, traced minimum width and traced maximum width of each particle were exported. The mean traced width was calculated as the average of the minimum and maximum widths. The smallest particles in the data had length 0.66 µm, 1.0 µm, and 2.0 µm for the IS60X, IS40X, and IS20X, respectively.

4.2 Samples

A summary of the samples used in this work is given in Table 4.2. The pulps (bleached and unbleached chemical, and thermo-mechanical) were chosen to give fines with different shapes and optical properties. The PCC was chosen to represent a common filler type. A mixed model stock was made by mixing 10% of PCC with 90% unbleached kraft softwood (UKSW), by weight.

The sizes of the silica spheres were selected to enable evaluation of the resolution of the instruments. The mixture of 20 and 80 nm spheres was chosen for the Mastersizer, the 350 nm and 2.0 µm spheres for the ImageStream, and the 7 µm spheres for the FT+. If sphere size was much smaller than the spatial resolution of an instrument, the spheres were not measured with that instrument. According to the manufacturers, the 350 nm silica spheres had been characterized by dynamic light scattering, while the size of the 2 µm and 7 µm spheres were characterized by electrozone sensing (Coulter Counter). The mixture of 20 nm and 80 nm spheres were characterized by dynamic light scattering, electron microscopy, and centrifugal liquid sedimentation.
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Abbreviation | Sample | Source | Measured with
--- | --- | --- | ---
BKHW | Bleached chemical HW, highly lab refined | Södra | MS, IS, FT, FT+
UKSW | Unbleached chemical SW, mill refined, SR = 16.8, kappa number = 51 | BillerudKorsnäs Frövi | MS, IS, FT, FT+
TMP | Thermo-mechanical pulp | N/A | MS, IS, FT, FT+
PCC | Precipitated calcium carbonate (Albacar LO), average diameter 2.2 µm | Specialty Minerals | MS, IS, FT, FT+
Mix | 10% PCC+ 90% UKSW | See above | MS, IS, FT, FT+
S20.80nm | Silica nanospheres Ø20 + Ø80 nm | JRC-IRMM | MS
S350nm | Silica nanospheres Ø350 nm | Microparticles GmbH | MS, IS
S2µm | Silica microspheres Ø2.0 µm | Microparticles GmbH | MS, IS
S7µm | Silica microspheres Ø7.0 µm | Microparticles GmbH | MS, IS, FT, FT+

Table 4.2. List of samples measured in this work.

Scanning electron microscopy (SEM) images of the PCC and S7µm samples are shown in Figure 4.8.

Figure 4.8. SEM micrographs samples. **Left:** Albacar LO PCC. **Right:** S7µm silica microspheres (courtesy of Joanna Hornatowska).

4.2.1 Screening

To obtain the fine fractions, the stock samples were screened in a Britt Dynamic Drainage Jar (BDDJ, see ISO-10376:2011 standard). To avoid excessive dilution, a modified BDDJ method with only one washing cycle instead of four was used. 0.5 g of dry pulp was added to 500 ml tap water. The suspension was poured into a BDDJ container equipped with a rotating propeller, and a fine screen with Ø76 µm holes. The suspension was dewatered through the screen and the fine fraction collected in a jar. A single wash of 500 ml was added, giving a total fine fraction volume of 1000 ml.

To evaluate the effect of the modification of the BDDJ method, a few screenings were also carried out with the standard 4 washing cycles. The fines content of the 1-wash procedure was compared to the fines content of the 4-wash procedure. It was found that approximately 2/3 of the fines were removed with a single wash. In order to evaluate if the morphology of the fines fraction changes with the number of washing cycles, three samples of the 1-wash and 4-wash suspensions, respectively, were measured with the ImageStream system at magnification 60X. It was expected that the more diluted 4-
wash suspension would contain fewer agglomerates, and more single long particles, as longer particles would have statistically more chances to align vertically against the screen and pass it. Correspondingly, the share of smaller particles would be slightly lower. Only minor differences in this respect were obtained in the results (Farahani 2015).

The relative composition of the mixed sample was changed by the screening. While only a small fraction of the pulp passed the mesh, the majority of PCC particles were small enough to pass. In the screened sample, the weight composition was roughly 85% PCC and 15% fines.

4.2.2 Estimation of the complex refractive index of fines

As previously mentioned, laser diffractometry requires that the refractive index of the sample is supplied to the analysis software. It is usually assumed that the refractive index of wood fibres is equal to that of cellulose; which is tabled as \( n = 1.55 \) (Thorn and Au 2009). However, it has been shown that the complex refractive index of cellulose, hemicellulose and lignin are all different from each other, and vary with wavelength (Bergström et al. 1999; Hollertz 2014). For example, at short wavelengths, the chromophores in lignin may impact the extinction coefficient in an unbleached pulp.

Refractive index values of cellulose, hemicellulose and lignin at three different wavelengths are given in Table 4.3. As the substances in Table 4.3 were measured at different relative humidity (RH), one needs to normalize them to their dry refractive index. Based on the literature, it appears that the influence of moisture on the refractive index of hemicellulose is similar to that of dry cellulose, resulting in the same dry refractive index, aside from a higher extinction coefficient for hemicellulose (Fink 1992). The refractive index of lignin is not significantly influenced by moisture content, as lignin is hydrophobic.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cellulose (~dry)</th>
<th>Hemicellulose (48% RH)</th>
<th>Lignin (48% RH)</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{466\text{nm}} )</td>
<td>1.55+0i</td>
<td>1.44+0.01i</td>
<td>1.63+0.03i</td>
<td>1.34+0i</td>
</tr>
<tr>
<td>( n_{633\text{nm}} )</td>
<td>1.52+0i</td>
<td>1.42+0.01i</td>
<td>1.59+0.01i</td>
<td>1.33+0i</td>
</tr>
<tr>
<td>( n_{785\text{nm}} )</td>
<td>1.51+0.005i</td>
<td>1.42+0.01i</td>
<td>1.58+0.005i</td>
<td>1.33+0i</td>
</tr>
</tbody>
</table>

Table 4.3. Complex refractive index of water and lignocellulosic compounds in dry state. Extinction coefficients below \( 10^{-3} \) were considered negligible.

In general, it is often overlooked how the refractive index changes with moisture content. A water-absorbing particle will have a different refractive index when wet, compared to a non-absorbing particle. By applying a volume-based mixing rule, one can estimate the refractive index of a wet particle (Jonasz and Fournier 2007):

\[
\tilde{n}_{\text{wetfibre}} = \frac{V_{\text{H}_2\text{O}}}{V_{\text{total}}} \tilde{n}_{\text{H}_2\text{O}} + \frac{V_{\text{dryfibre}}}{V_{\text{total}}} \tilde{n}_{\text{dryfibre}}
\]

[Eq. 1.8]

where \( V \) is the volume of the substance in a particle. For the calculation, the water content of the particle must be estimated. Kraft fibres in a suspension hold around 1.2 cm\(^3\) water per 1 g fibre material, while TMP holds around 0.6 cm\(^3\)/g (Subramanian...
et al. 2008). The density of water and kraft fibres are 1.0 g/cm$^3$ and 1.5 g/cm$^3$, respectively (Lee 1992). Using the general values of $n_{\text{dry fibre}} = 1.55$ and $n_{\text{H}_2\text{O}} = 1.33$, would give $n_{\text{wet fibre}} = 1.41$ for a wet kraft fibre.

For an optimal analysis of laser diffractometry data, the extinction coefficient should also be known. It is then insufficient to use the general value for fibres, as the extinction coefficient is not specified. A more detailed calculation of the complex refractive index of fibres may be performed by again applying a mixing rule:

$$
\bar{n}_{\text{dry fibre}} = \frac{V_{\text{cellulose}}}{V_{\text{total}}} \bar{n}_{\text{cellulose}} + \frac{V_{\text{hemi}}}{V_{\text{total}}} \bar{n}_{\text{hemi}} + \frac{V_{\text{lignin}}}{V_{\text{total}}} \bar{n}_{\text{lignin}} \tag{Eq. 1.9}
$$

The complex refractive index of cellulose, hemicellulose and lignin are given in Table 4.3. The volume shares of the different compounds are given in Table 4.4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.5 g/cm$^3$</td>
<td>1.5 g/cm$^3$</td>
<td>1.3 g/cm$^3$</td>
</tr>
<tr>
<td>Share in BKHW fibre</td>
<td>70%</td>
<td>27%</td>
<td>3%</td>
</tr>
<tr>
<td>Share in UKSW fibre</td>
<td>67%</td>
<td>25%</td>
<td>8%</td>
</tr>
<tr>
<td>Share in TMP fibre</td>
<td>35%</td>
<td>30%</td>
<td>35%</td>
</tr>
</tbody>
</table>

Table 4.4. Density of the fibre compounds (Boyer and Rudie 2007) and mass composition of the pulp samples used in this work (Subramanian et al. 2008; Östlund 2015). Due to the similar densities of the compounds, the mass and volume compositions are close to equal.

It has been shown that fines can hold more water than fibres; 4.3 cm$^3$/g for kraft fibrils, and 1.3 cm$^3$/g for TMP fines (Subramanian et al. 2008). Assuming that only the bulk water contributes to the volume, and not the non-freezing bound or freezing bound water, the density becomes 1.1 g/cm$^3$ for wet kraft fines, and 1.3 g/cm$^3$ for wet TMP fines. Finally, the volume share becomes 78% water and 25% fibre material for wet kraft fines, and 63% water and 37% fibre material for wet TMP fines.

Accounting for all these factors when applying the volume-based mixing rule gives the refractive indices shown in Table 4.5.

<table>
<thead>
<tr>
<th></th>
<th>Dry</th>
<th></th>
<th>Wet</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BKHW</td>
<td>UKSW</td>
<td>TMP</td>
<td>BKHW</td>
</tr>
<tr>
<td>$\bar{n}_{466nm}$</td>
<td>1.55±0.002i</td>
<td>1.56±0.004i</td>
<td>1.58±0.001i</td>
<td>1.37±0i</td>
</tr>
<tr>
<td>$\bar{n}_{633nm}$</td>
<td>1.52±0.002i</td>
<td>1.53±0.002i</td>
<td>1.54±0.006i</td>
<td>1.37±0i</td>
</tr>
<tr>
<td>$\bar{n}_{785nm}$</td>
<td>1.51±0.006i</td>
<td>1.52±0.006i</td>
<td>1.53±0.006i</td>
<td>1.37±0.001i</td>
</tr>
</tbody>
</table>

Table 4.5. Calculated complex refractive index of fibres and fines in the pulps used in this work. Extinction coefficients below 10$^{-3}$ were considered negligible.

**4.2.3 Estimation of the complex refractive index of fillers and silica spheres**

Tabled refractive indices for PCC ranges between 1.56 (Eklund and Lindström 1991) and 1.61 (Pauler 1999). In this work, a value of 1.59 was used (Koivunen et al. 2009). It was not possible to find literature values on the measured extinction coefficient of PCC or other papermaking fillers. Koivunen (2011) estimated the extinction coefficient of
handsheets with 20% PCC to be $10^{-5} < \kappa < 10^{-4}$. Thus, in this work, the extinction coefficient of PCC will be assumed to be negligible.

Little is published on the absorption of water by papermaking fillers. As long as the filler is not too porous, it should not absorb water and its wet refractive index should remain close to its dry value. Consequently, the optical difference between papermaking particles is much larger when suspended in a stock, than in a dry paper sheet. The large difference in refractive index between fillers and fines then becomes a problem in laser diffractometry measurements of a mixed stock, as it is only possible to set a single refractive index.

As previously mentioned, it is estimated that, after screening, the mixed sample consists of 85% PCC and 15% wet UKSW fines, by mass. The density of the PCC was 2.7 g/cm$^3$ (Hirvikoski 2015), and the density of wet kraft fines was previously calculated as 1.1 g/cm$^3$. A volume-based mixing rule then yields a refractive index of $n_{\text{mix,wet}} = 1.53 + 0i$. As most mixing rules are developed for inhomogeneous particles rather than two particle populations with different scattering properties, its application is associated with some uncertainty. For example, the particle size distribution of the respective particle population could influence the result (Jonasz and Fournier 2007). However, a similar approach was used in a study of soils, which found the results to be satisfactory (Eshel et al. 2004).

It was difficult to find a unanimous value for the refractive index of silica micro- and nanospheres. This was surprising, as several manufacturers offer them as calibration material, and such materials tend to be well-characterized. Recent studies report refractive index values between 1.41 and 1.43 (Zölls et al. 2013; Toitoki et al. 2015), while older studies report values between 1.45 and 1.46 (Malitson 1965). In this work, a value of 1.43 was used. The extinction coefficient of silica microspheres has been reported to be negligible (Malitson 1965; Toitoki et al. 2015).

### 4.3 Analysis of the measurement results

All measurement data was imported to Matlab, where the final calculations and evaluation were made. The following procedures were performed: (1) particle selection, (2) weighting, (3) calculation of additional parameters, (4) calculation of histograms, and (5) conversion to sphere-equivalent-diameter.

#### Particle selection

Image analysis standards define fines as particles smaller than 200 µm. However, some particles passing the Ø76 µm BDDJ mesh are larger than that, e.g. flexible fibres or fibre fragments. Thus, two analyses were made; one where particles longer than 200 µm were excluded, and one where all particles were included. The first analysis was used to compare the imaging methods, while the second analysis was used when laser diffractometry was compared with the image-based method, as the same size limit could not be imposed on the Mastersizer data.

#### Weighting

The raw data from all the imaging instruments was number-weighted, while for the laser diffractometry, it was volume-weighted. Length-, area-, and volume-weighting
were performed on all parameters from the imaging instruments. When calculating the volume $V$ for the volume-weighting, a cylindrical particle shape was assumed:

$$V = \frac{\pi}{4} W^2 L \quad \text{[Eq. 1.10]}$$

where $W$ and $L$ are the width, i.e. the diameter, and the length of the particle. For the stock samples, it was decided to use area-weighted data in the comparison between the imaging instruments. As the number of fines increases with decreasing size, number-weighting would suppress the larger particles in the distribution. Additionally, the bonding area is believed to play a role for the strength-enhancing properties of the fines, making area a relevant aspect to highlight.

For the silica spheres, it was decided to use number-weighting in the comparison between the imaging instruments, as this was believed to best correspond to the sizing methods used by the manufacturers.

When comparing with laser diffractometry, volume-weighting was used for all sample types.

**Calculation of additional imaging parameters**

From the FT and FT+, the rectangle-equivalent length and width were available. The area and the perimeter, i.e. the original base parameters for the FT and FT+, were reversely obtained from the length and the width using Eq. 1.5. Based on examination of the data, the offset was estimated to around 16% of the width. The rectangle-equivalent aspect ratio $AR$ was calculated as

$$AR_{RE} = \frac{L_{RE}}{W_{RE}} \quad \text{[Eq. 1.11]}$$

If a calculated aspect ratio was less than one due to the calibration offset to the width, the value was changed to one.

From the ImageStream, traced length and width, and area and perimeter were available. The area and the perimeter were used to calculate the rectangle-equivalent length and width, according to Eq. 1.6. The traced aspect ratio was calculated in the same way as Eq. 1.11.

As rectangle-equivalent parameters could be obtained for all the methods, it was decided that they would form the basis of the comparison between the imaging instruments. In addition, the difference between rectangle-equivalent and traced values would be investigated with the ImageStream data.

**Histogram calculation – comparison between imaging instruments**

Histogram distributions were calculated for the length, width and aspect ratio for each instrument. The bin widths for the length and width were chosen to reflect the resolution of the instruments, see Table 4.6. As the aspect ratio is calculated from the length and width, it exhibits a different range of values, and using similar bin width would impart a jagged shape on the curve. Instead, a larger bin width was used.
Table 4.6. Specifications for the measurements with the different instruments including bin width and size ranges for the histogram calculation. The values of the measured range are number-weighted.

In order to obtain comparable results even when data with different binning is plotted in the same graph, relative density histograms were calculated. The more common relative frequency histogram is produced by dividing the number of particles in each bin, $N_i$, by the total number of particles, $N_{tot}$:

$$N_{relative,i} = \frac{N_i}{\sum_{i=1}^{N} N_i} = \frac{N_i}{N_{tot}}$$  \hspace{0.5cm} [Eq. 1.12]

where $N_{relative,i}$ is the share of particles in bin $i$, in relation to the total number of particles. Relative density histograms are produced by also dividing by the bin width:

$$N_{density,i} = \frac{N_i}{binwidth \sum_{i=1}^{N} N_i} = \frac{N_i}{binwidth \times N_{tot}}$$ \hspace{0.5cm} [Eq. 1.13]

In a relative density histogram, the area of the histogram bins sums to one, or 100%, if expressed as percent, and allows for the comparison of distributions with a difference in bin width. An example of the difference between a frequency and a density histogram is shown in Figure 4.9:

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>IS60X</td>
<td>Instrument range</td>
<td>0.33-170</td>
<td>0.33-40</td>
<td>1-515</td>
</tr>
<tr>
<td></td>
<td>Measured range</td>
<td>0.66-84.66</td>
<td>0.33-26</td>
<td>1.0-26.8</td>
</tr>
<tr>
<td></td>
<td>Used bin width</td>
<td>2.0</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>IS40X</td>
<td>Instrument range</td>
<td>0.5-256</td>
<td>0.5-60</td>
<td>1-512</td>
</tr>
<tr>
<td></td>
<td>Measured range</td>
<td>1.0-70.5</td>
<td>0.5-19</td>
<td>1.0-22.2</td>
</tr>
<tr>
<td></td>
<td>Used bin width</td>
<td>3.0</td>
<td>3.0</td>
<td>1.0</td>
</tr>
<tr>
<td>IS20X</td>
<td>Instrument range</td>
<td>1-512</td>
<td>1.0-120</td>
<td>1-512</td>
</tr>
<tr>
<td></td>
<td>Measured range</td>
<td>2-72</td>
<td>1.0-36</td>
<td>1.0-13.5</td>
</tr>
<tr>
<td></td>
<td>Used bin width</td>
<td>6.0</td>
<td>6.0</td>
<td>1.0</td>
</tr>
<tr>
<td>FT+</td>
<td>Approx. instrument range</td>
<td>4-9000</td>
<td>4-9000</td>
<td>1-1250</td>
</tr>
<tr>
<td></td>
<td>Measured range</td>
<td>4-1141</td>
<td>3.6-68.4</td>
<td>1.0-82.4</td>
</tr>
<tr>
<td></td>
<td>Used bin width</td>
<td>4.0</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>FT</td>
<td>Approx. instrument range</td>
<td>10-13000</td>
<td>10-13000</td>
<td>1-1250</td>
</tr>
<tr>
<td></td>
<td>Measured range</td>
<td>15-4131</td>
<td>9.1-78.2</td>
<td>1.0-136.5</td>
</tr>
<tr>
<td></td>
<td>Used bin width</td>
<td>10.0</td>
<td>10.0</td>
<td>1.0</td>
</tr>
<tr>
<td>All instruments</td>
<td>Used histogram range</td>
<td>[resolution]-200</td>
<td>[resolution]-70</td>
<td>1-50</td>
</tr>
</tbody>
</table>
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Figure 4.9. Examples of different histograms. Left: Relative frequency histogram distribution. Right: Relative density histogram distribution.

Curve plots were obtained from the histogram values using the leftmost point each bin as the x-value, see Figure 4.10. To illustrate the bin widths without creating a complicated graph, markers are shown only for the first two data points. As it is not well shown in the curve plot, it is important to remember that the points do not represent the centre of the bins.

Figure 4.10. Example of how data points are taken from a relative density histogram to produce curve plots. Left: Histogram bins and data points. Right: Final curve.

**Conversion to circle- and sphere-equivalent diameter**

In order to compare the measured size of the silica spheres to the diameter provided by the manufacturer, the circle-equivalent diameter (CED) was calculated from the imaging instrument data.

\[
CED_{\text{circle}} = \left( \frac{4A}{\pi} \right)^{1/2} \tag{Eq. 1.14}
\]

where \(A\) is the area. For a sphere, the circle-equivalent diameter is the same as the sphere-equivalent diameter (SED). That is not the case for a cylinder, e.g. an idealized
fines particle. To compare laser diffractometry data to imaging data, the SED must be calculated from the imaging parameters. Assuming a cylindrical particle shape, the CED and SED are given by Eq. 1.15.

\[
\begin{align*}
\text{CED}_{\text{cylinder}} &= \left( \frac{4LW}{\pi} \right)^{1/2} \\
\text{SED}_{\text{cylinder}} &= \left( \frac{3}{2} W^2 L \right)^{1/3}
\end{align*}
\]  

[Eq. 1.15]

Histogram calculation – comparison with laser diffractometry

The Mastersizer data comprised 50 logarithmically spaced values ranging from 0.02 µm to 1000 µm. To obtain comparable data from the imaging instruments, volume-weighted SED was calculated, and a relative frequency distribution was calculated using the same logarithmically spaced values. The data was plotted on a logarithmic x-axis, see right side of Figure 4.11.

![Figure 4.11](image_url)  
Figure 4.11. How data points from logarithmically spaced histograms are taken to produce curve plots. **Left:** Linearly spaced x-axis. **Right:** logarithmically spaced x-axis.
5 Results and discussion

5.1 Part 1 - Result of instrument verification

In the following section, the results of the instrument verifications are presented. Using the monodisperse silica micro- and nanospheres with refractive index similar to wet fibre material, the resolution, accuracy, and uncertainty due to particle motion were evaluated for the different instruments. A summary of the results of the verification is given in Table 5.1, and additional details are provided in the following sections.

<table>
<thead>
<tr>
<th>Sample Instrument</th>
<th>S20nm</th>
<th>S80nm</th>
<th>S350nm</th>
<th>S2.0µm</th>
<th>S7.0µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IS60X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IS40X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IS20X</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FT+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FT</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


5.1.1 Verification – Mastersizer

The results of the MS measurements of the silica spheres are given in Table 5.2. Additional quantitative data can be found in Table A 1 in the Appendix.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S80.20nm</th>
<th>S350nm</th>
<th>S2.0µm</th>
<th>S7.0µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specification</td>
<td>20 ±4nm</td>
<td>350 ±20nm</td>
<td>2.06 ±0.05µm</td>
<td>7.00 ±0.29µm</td>
</tr>
<tr>
<td>Measured SED</td>
<td>106</td>
<td>355</td>
<td>2.02</td>
<td>7.84</td>
</tr>
<tr>
<td>Span</td>
<td>±810 nm</td>
<td>±586 nm</td>
<td>±0.58 µm</td>
<td>±1.50 µm</td>
</tr>
<tr>
<td>Relative error</td>
<td>N/A</td>
<td>32%</td>
<td>1%</td>
<td>2%</td>
</tr>
</tbody>
</table>

Table 5.2. Laser diffractometry measurements of silica spheres, with relative error compared to manufacturer’s specification.

The MS had a mixed performance when measuring on the silica spheres. The S350nm and S2µm samples were sized with high accuracy, but the S350nm had a wide span. The measurements of the S20.80nm and S7µm samples had large relative errors and wide spans, which can be explained by the particle size distribution, see Figure 5.1. Here, it can be seen that the 20 nm spheres were not detected at all; implying that laser diffractometry cannot be used to characterize nanocellulose aggregates, where 20 nm is a common width. The wide span for the S80.20nm sample also implies that the uncertainty would be high for particles around 80 nm. Another observation is that the S7µm sample exhibited an unexpected peak at 1.5 µm, which was present even at repeated sampling and re-measurement. As will be seen in the image analysis section below, there is no indication of its presence there. Thus, it is at this point regarded as a potential ghost peak (e.g. Sabin 2011).
5.1.2 Verification – Imaging instruments

A wide range of parameters were calculated from the imaging data of the silica spheres. Some are presented in this section, and the others are tabled in Tables A 2, A 3, and A 4 in the Appendix. As mentioned in the method section, the S350nm and S2μm samples were measured only with the ImageStream, while the S7μm sample was measured with all the imaging instruments. The particles are exemplified in Figure 5.2.

**Figure 5.2.** The silica spheres as imaged by the ImageStream.

**Resolution**

The number of analysed particles was used to validate the resolution of the instruments, see Table 5.3.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Spatial resolution</th>
<th>Number of analysed particles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>S350nm</td>
</tr>
<tr>
<td>IS60X</td>
<td>0.33 μm/pix</td>
<td>13082</td>
</tr>
<tr>
<td>IS40X</td>
<td>0.5 μm/pix</td>
<td>10744</td>
</tr>
<tr>
<td>IS20X</td>
<td>1.0 μm/pix</td>
<td>223</td>
</tr>
<tr>
<td>FT+</td>
<td>4 μm/pix</td>
<td>N/A</td>
</tr>
<tr>
<td>FT</td>
<td>10 μm/pix</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*Table 5.3.* Number of particles shorter than 200 μm in “Single particles in focus” population (IS60/40/20X), or measured during 20 minutes measurement time (FT/FT+).

Based on the number of analysed particles, the IS60X and IS40X detected the S350nm particles, while the IS20X did not. It was a surprise that the IS40X detected particles...
with a size well below its spatial resolution. The most likely explanation is that the
detected particles were enlarged due to out-of-focus positioning or optical aberrations.
Ideal positioning of the particle relative to the pixels, which should occur randomly,
may also contribute.

All three IS magnifications detected the S2µm particles. The lower count was due to
high sample concentration, resulting in more images containing multiple particles that
were not included in the analysis population.

All instruments seem to have detected the S7µm particles. However, as seen in the
following section, the accuracy was poor for the FT.

Accuracy

All instruments greatly overestimated the size of the spheres, compared to the
manufacturers’ specified sizes. The measured circle-equivalent diameter (CED) of the
S7µm sample is shown in Figure 5.3.

![Figure 5.3. CED distribution of S7µm particles shorter than 200 µm, measured with different imaging instruments. Left: Number-weighted. Right: Area-weighted. Dotted vertical line = diameter specified by the manufacturer.](image)

The relative overestimation was larger when the particle size was closer to the
resolution of the instrument, see Table 5.4. As mentioned in the background section, the
positioning error introduced by the alignment of the particle relative to the pixel grid
(on the pixel centre or on a vertex) is large when the particle size is close to the pixel
size. Additionally, in the case of ImageStream, the “Sample” segmentation algorithm
removes the 1-pixel objects, leaving the larger objects and resulting in an overall larger
mean size.

<table>
<thead>
<tr>
<th>Relative error</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
<th>FT+</th>
<th>FT</th>
</tr>
</thead>
<tbody>
<tr>
<td>S350nm</td>
<td>157%</td>
<td>185%</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S2µm</td>
<td>30%</td>
<td>65%</td>
<td>85%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>S7µm</td>
<td>39%</td>
<td>33%</td>
<td>21%</td>
<td>24%</td>
<td>242%</td>
</tr>
</tbody>
</table>

Table 5.4. Relative error in measured, number-weighted CED of silica micropsheres, compared to manufacturer’s specification.
Influence of segmentation

It was seen that the particle size was overestimated when their size was close to the spatial resolution of the instrument. However, the S7µm particles were also oversized; even by the IS which had resolutions well above their size. In order to investigate possible causes, a few different segmentation algorithms were tested, see Figure 5.4. It is evident that the measured size is highly influenced by the segmentation algorithm. The “Sample” segmentation algorithm, which was developed for fines analysis, struggles to capture the edges of the particle due to a bright halo. The halo is caused by diffraction, which gets stronger for larger particles and high refractive indices. This implies that the optical properties of the silica spheres are still too far from those of fines to constitute a good calibration material.

Figure 5.4. IS60X images of S7µm particles, showing influence of segmentation algorithm on measurement result. Blue numbers show the CED. None: No segmentation. Default: Default algorithm. Sample: Algorithm used in this work, adapted for fines (see method section). Erode X: Default mask eroded by X pixels.

Influence of particle motion

When inspecting the images, it was clear that they had been obtained at a wide range of (auto)foci, see Figure 5.5. Furthermore, it could be seen that the foci differences influenced the measured size.

Figure 5.5. Examples of range of foci found in ImageStream measurements of silica spheres. The value of circle-equivalent diameter (CED) is shown in blue.

The effect of focus on the mean size can be assumed to be low, with similar share of particles being over-sized as under-sized. However, it is reasonable to assume that, for monodisperse samples like the silica spheres, a large part of the standard deviation originates from particle motion in the depth direction; i.e. out of the focal plane.

For the S350nm particles measured with the IS60X, the standard deviation was around 25% of the measured value. For the S2µm, it was around 20% for the IS60X, 30% for the IS40X, and 50% for the IS20X. For the S7µm sample, the standard deviation was
10-15% of the measured value for IS20X/40/60X and FT+, and around 100% for the FT. A standard deviation of 10% can be acceptable in particle size analysis (Plantz 2006; Horiba 2015), while a value above 20% is likely unacceptably high.

5.1.3 Verification – instrument comparison

The S7µm sample was the only microsphere sample measured with all instruments. No upper limit on particle size was set in the calculation. The SED distributions from the different instruments are shown in Figure 5.6, and the quantitative mean values are given in Table A 5 in the Appendix.

**Figure 5.6.** SED distribution (volume-weighted) of the S7µm sample measured by the different instruments.

The distributions from the different instruments show a high degree of alignment, with the exception of the FT. The FT was set to measure on 60 000 fibres or until 20 minutes had passed, and continued for the full 20 minutes as not enough particles fulfilling the criteria for fibres were detected. During this time, approx. 20 000 particles were detected. As was seen in Figure 5.3, the majority of these particles were 15 µm objects; the shortest length found in FT data. However, some detected particles were much larger; sufficient to suppress the 15 µm particles when volume-weighting was applied. The nature of these objects could not be confirmed. Possible candidates are particles that linger in the system from previous measurements (“carryover”) even after the automated cleaning performed by the instrument. The results imply that measurements on pure water should be made complimentary to the sample measurements, in order to estimate this effect.

The unexpected peak in the S7µm MS data (Figure 5.1) was not observed for any other silica sample, or for any of the other measurement instruments. This strengthens the explanation that the peak was a diffraction ghost artefact.
5.2 Part 2 – Measurements and comparison on fine fractions

In the following section, the performance of the instruments on pure and mixtures of papermaking particles is presented.

5.2.1 Fine fractions - Mastersizer

The quantitative data of the MS measurements on the pure and mixed fines fractions are given in Table A 6 in the Appendix. The particle size distributions of the pure fines samples are shown in Figure 5.7.

![Figure 5.7. Left: SED distribution (volume-weighted) measured the Mastersizer on pure fines samples. Right: Calculated SED for a cylinder of varying length and width.](image)

Only minor differences between the fines samples were detected. The TMP fines have a wider distribution and a larger share of small particles, when compared to the unbleached and bleached kraft fines samples.

It is surprising that none of the samples exhibit a share of particles below ~3 µm. With a resolution of at least 80 nm verified with the silica spheres, it can be expected that some sub-micron material would be seen. One possible explanation for the absence of small particles is that the SED of a cylindrical particle underestimates its length and overestimates its width, as shown in the right side of Figure 5.7. For example, a fibril of width 0.2 µm and length 10 µm would have a SED of around 0.5 µm. However, this would not explain why particles with sizes 0.5-3.0 µm are not seen in the distribution. Another possible explanation is the volume-weighting, which suppresses the smaller particles and enhances the larger. A combination of these explanations was proposed in a study where laser diffractometry was used to measure on cellulose nanofibrils (CNF) (Gamelas et al. 2015). In that study, the minimum observed sizes were 2-6 µm.Regrettably, the refractive index used to obtain the data was not stated.

In the present study, evaluating the data using the other optional (and not recommended) weightings in the Mastersizer analysis software did not change the minimum size of the distribution, see Figure 5.8. Neither did restricting the maximum size change the minimum size. This shows that, while the volume-weighting suppresses the smaller particle so that the shape of the distribution changes, it does not suppress them to the degree that they become unnoticeable.
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Figure 5.8. Weighting and upper size limit variations in the MS analysis. **Left:** UKSW sample evaluated using the number-, length, surface area-, and volume-weighting options in the MS analysis software. **Right:** UKSW sample evaluated using the size exclusion option.

A final possibility is that the intensity of the diffracted light drops below the detection limit of the instrument as the size decreases. The intensity of the diffracted light is dependent on both the size of the particle and its refractive index contrast relative to the surrounding water (see Eq. 1.1). For fines, this contrast is low, while for fillers, it is higher. It is also seen in the right side of Figure 5.9 that the PCC exhibits lower minimum size; around 1.5 µm. In a study where laser diffraction was used to measure on fractionated cellulose microfibrils, sub-micron average sizes were reported (Haapala et al. 2013). However, no size distribution was provided, nor the value of the refractive index used to obtain the data. As seen in the left side of Figure 5.9, using a too high or too low value of the refractive index can create artificial peaks at lower sizes, which could explain lower reported sizes.

Figure 5.9. SED distribution (volume-weighted) measured with the Mastersizer. **Left:** UKSW fines evaluated using different refractive index and extinction coefficient. **Right:** Pure UKSW fines, pure PCC, and mixture of the two, evaluated at different refractive indices.
5.2.2 Fine fractions – Imaging instruments

The quantitative data of the image-based measurements on the pure and mixed fines fractions are given in Table A 7 in the Appendix. The length, width, and aspect ratio distributions of two of the samples are shown in Figure 5.10, Figure 5.11, and Figure 5.12.

**Figure 5.10.** Length distribution (area-weighted) of particles shorter than 200 µm, measured with different imaging instruments. Note that the y-axis scales are different. **Left:** UKSW fines. **Right:** Mixture of UKSW fines and PCC.

**Figure 5.11.** Width distribution (area-weighted) of particles shorter than 200 µm, measured with different imaging instruments. **Left:** UKSW fines. **Right:** Mixture of UKSW fines and PCC.
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Figure 5.12. Aspect ratio distribution (area-weighted) of particles shorter than 200 µm, measured with different imaging instruments. Left: UKSW fines. Right: Mixture of UKSW fines and PCC.

Qualitatively, the distributions in Figure 5.10 to Figure 5.12 are fairly similar, in that the relative share of particles increases with decreasing size, for all instruments except the FT. Quantitatively, the IS detects a much higher share of small particles, which go undetected by the FT+ and FT due to their coarser resolution. The observation opens up the question if the amount of fines continues to increase with decreased size down to the elementary fibril, or if the fines creation process favours a certain size and shape that would create a peak in the data. Here, additional studies on fines creation during refining and quantitative studies using higher-resolution instruments would provide valuable knowledge.

An implication is that the resolution of a fibre analyser will greatly influence the measured fines content, as it is based on the number of detected fines particles compared to either the number of fibres or the number of fines plus fibres. A higher resolution will give a higher fines content value.

The two populations in the mixed sample, i.e. the fines and fillers, are not distinguishable from each other in the distributions. It is expected that the fines and fillers have different shapes (flaky and fibrillar vs. round/scalendohedral). However, neither size (length, width) nor shape (aspect ratio) appears to be sufficient for separating between the particle types. This is likely a combined influence of the dominating PCC population, and the similar size and shape of PCC and small fines. It is possible that volume-weighting can accentuate the shape-based differences, especially for the polydisperse fines, which should then be observed in the next section.
5.2.3 Fine fractions – Instrument comparison

Quantitative values of the mean SED are tabled in Table A 10 in the Appendix. The 200 µm upper limit on particle size was not used when comparing all the instruments, and large particles that passed through the Ø76 µm BDDJ mesh, e.g. fibre fragments, may thus be present in the data.

Pure fines

Volume-weighted SED distributions comparing all the instruments are given in Figure 5.13 (BKHW), Figure 5.15 (TMP) and Figure 5.14 (UKSW). Some example images from the IS60X measurements are shown, which should however not be considered representative for the entire sample. The CED given in the images is number-weighted, as this was the only weighting that was available in the image export tool.

BKHW

![BKHW SED distribution](image)

**Figure 5.13.** BKHW fines. **Top:** SED distribution (volume-weighted) for all measurement instruments. **Bottom:** Images from IS60X measurements, with number-weighted CED given in blue. Note that the length of the scale bar is different for each image.
**UKSW**

![UKSW fines](image)

**Figure 5.14.** UKSW fines. **Top:** SED distribution (volume-weighted) for all measurement instruments. **Bottom:** Images from IS60X measurements, with number-weighted CED given in blue. Note that the length of the scale bar is different for each image.

**TMP**

![TMP fines](image)

**Figure 5.15.** TMP fines. **Top:** SED (volume-weighted) distribution for all measurement instruments. **Bottom:** Images from IS60X measurements, with number-weighted CED given in blue. Note that the length of the scale bar is different for each image.
Again, it can be seen that the impression of a measured sample is highly dependent on the resolution and field-of-view of the measurement instrument. The MS data correlates with the FT data. These instruments have the largest field-of-view. The FT+ and IS20X, which have intermediate resolutions and field-of-views, partly bridge the gap between the MS/FT and IS60X/IS40X data.

The IS40X and IS60X exhibit data at smaller sizes, which is not present in the MS data. This is both an effect of the high resolution, and a selection effect. Since the amount of particles increases with decreased size, a higher resolution will yield a higher share of small particles in the data. Additionally, the field-of-view of the IS60X and IS40X is much more limited than the MS (see Table 4.1), preventing the detection of larger particles. The larger particles would significantly skew the distribution towards large sizes, and suppress the small particles.

The discrepancy between the MS and IS data at small sizes could also be explained if the refractive index of wet fines is lower than that estimated in the method section. As seen in Figure 5.9, using a lower refractive index would create an additional peak in the laser diffractometry data, at lower sizes where particles are “missing”. However, the additional peak would not overlap with the peaks of the imaging data, but instead appear at lower sizes. Thus, they could simply be interference effects from the Mie theory model.

As previously suggested, another possible explanation is that small fines scatter too little light by diffraction to be detected by the MS. The idea is supported by the results for the TMP fines. TMP fines, which are known to be good light scatterers, exhibit particles from ~3 µm in the MS data, while the BKHW and UKSW fines exhibit particles from ~8 µm.
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**PCC**

![Graph showing SED distribution for different measurement instruments](image)

**Figure 5.16.** PCC fine fraction. **Top:** SED distribution (volume-weighted) for all measurement instruments. **Bottom:** Images from IS60X measurements, with number-weighted CED given in blue. Note that the length of the scale bar is different for each image.

As seen in the IS60X images, the PCC sample comprises both single particles, which are spherical on a macroscopic level, and agglomerated structures of different sizes. The MS results showed that that 10% (volume-share) of the PCC had sizes below 2 µm, 50% below 4.0 µm, and 90% below 7.0 µm (see Table A 6 in the Appendix). Thus, the IS should be able to resolve a significant share of the single PCC particles, which is also confirmed by the images above. To our knowledge, this is the first time that characterization of single filler particles by a flow microscope is reported. The FT+ spatial resolution (~4 µm) allows for detection of only the largest single PCC particles, and the instrument will mostly measure agglomerates and large fines. Correspondingly, the FT (resolution ~10 µm) should only detect agglomerates.

For PCC, there is a higher compliance between the MS and the imaging data than what was observed for the fines samples. The exception is the FT, whose distribution looks similar to that in *Figure 5.6* and likely measures a combination of PCC agglomerates and the previously proposed carryover. The compliance further strengthens the idea that detection of small particles by the MS requires high refractive index difference between the sample particles and the water suspension.

Finally, it is notable that the IS40X and IS60X seem to perform equally well as the MS in detecting the PCC particles. Judged by the SEM images and the MS data, the PCC evaluated in this work is rather coarse. If the same study was made on a finer PCC, it is possible that the IS resolution would be insufficient for a good measurement performance.
Mix

**Figure 5.17.** Fine fraction of mixture of UKSW and PCC. **Top:** SED distribution (volume-weighted) for all measurement instruments. **Bottom:** Images from IS60X measurements, with number-weighted CED given in blue. Note that the length of the scale bar is different for each image.

The MS and FT+ distributions of the mixed sample exhibit a bimodal shape, which is expected. The peak around 30 µm corresponds to the peak in the pure UKSW data (see Figure 5.14). The PCC peak in the MS data is surprisingly small given that the PCC constitutes ~80% of the volume of the sample. The results may be explained by the polydisperse size distribution of the fines, compared to the narrower distribution of the PCC. Some fines particles will be significantly larger than the others. When weighted by their volume, these few particles will push the distribution towards large values. If the composition of the sample had been 85% fines and 15% PCC, by volume, the PCC would likely not have been seen.

It is difficult to distinguish modes in the IS data due to the jagged shape of the curve, but it does not have a clear bimodal shape. Comparing the pure UKSW and pure PCC distributions (Figure 5.14, Figure 5.16), it can be seen that IS data from the two pure samples overlaps in size. The conclusion is that it is not possible to separate between single PCC particles and single fines particles based on their size alone. Here, the light-scattering and fluorescence detectors of the ImageStream could provide an alternative approach.
6 Conclusions

Two classes of optical instruments were compared: diffraction-based and image-based. The prerequisite of the chosen instruments was that they should be commercially available and able to measure on a flowing suspension. The compared instruments were the Mastersizer2000 (MS) from Malvern, based on the laser diffractometry principle, the ImageStream (IS) from Amnis, and the L&W Fiber Tester (FT) and L&W Fiber Tester Plus (FT+) from Lorentzen & Wettre, all three based on imaging principles. The imaging instruments had spatial resolutions ranging from 0.33 µm to approximately 10 µm per pixel.

The instruments were evaluated using monodisperse silica micro- and nanospheres with optical properties similar to wet fibres, and on fine fractions from pure and mixed model stocks. The difference in refractive index of wet fines, compared to dry fibres, was estimated and accounted for. Relative measurement errors were estimated based on the measurements on the silica spheres.

Based on the evaluation, instrument recommendations for the size characterization of samples used in papermaking are summarised in Table 6.1.

<table>
<thead>
<tr>
<th>Sample Instrument</th>
<th>Pulp (fibres + fines)</th>
<th>Pure fibres</th>
<th>Pure fines</th>
<th>Pure fillers</th>
<th>Fines-filler mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>Red</td>
<td>Red</td>
<td>Green</td>
<td>Red</td>
<td>Green</td>
</tr>
<tr>
<td>IS60X</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
</tr>
<tr>
<td>IS40X</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
</tr>
<tr>
<td>IS20X</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
</tr>
<tr>
<td>FT+</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
<td>Green</td>
</tr>
<tr>
<td>FT</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Yellow</td>
</tr>
</tbody>
</table>


The MS failed to detect the 20 nm silica spheres and oversized the 100 nm spheres. All imaging instruments overestimated the size of the different spheres, with relative errors ranging from 21% to 185%. It was found that the imaging measurement result was highly sensitive to the choice of segmentation algorithm. Thus, a more complete uncertainty analysis would require investigation of the FT+ segmentation algorithm, which was not available in this work. While care had been taken to choose the best calibration material, the optical properties of the silica spheres were too dissimilar from those of wet fines. If nanocrystalline cellulose could be manufactured as a monodisperse, micron-sized sample, it would likely pose a better calibration material. It was also noted that pure water samples should be included in a measurement series to quantify possible carryover of particles from previous measurements, or particles in the dilution water.

In theory, the major strength of laser diffractometry is its high resolution and wide size range. However, in practice, it did not perform better than the IS or the FT+. Fines particles smaller than about 3 µm were not detected. A suggested explanation was that small particles with a refractive index close to that of water, which is the case for
highly-swollen fines, diffracted too little light to reach above the noise level of the instrument. The obtained result was also highly sensitive to the choice of refractive index; a fact that some of the previous users apparently were not aware of. It is concluded that laser diffractometry measurements on fines and fines-filler mixtures are unreliable.

For the imaging instruments, the measurement result was heavily influenced by resolution and field-of-view. With increased resolution, the share of small particles was higher, which implies that a fairly large share of particles exist that can only be detected with a sufficiently high resolution. The IS resolved single PCC particles, which has previously not been possible using flow imaging, as well as fines that were not detected by neither the FT nor the FT+. However, due to a limited measurement area, the IS was not able to measure the largest fines, which also increased the quantitative value of the share of the smaller fines. As the larger fines can be analysed with the FT+, the two instruments were found to be complimentary. However, measurements with the IS take much more time as all larger particles have to be removed in order not to cause a plugging of the equipment.

It was found that the information on size and shape were not sufficient to differentiate between fines and fillers particle in the mixed sample. However, additional optical signals such as single particle light-scattering and fluorescence in the IS proved to be useful for this purpose. Promising results related to that approach were obtained in a recently performed final thesis at Innventia (Sarakinis 2015). This approached should definitively be pursued. Also, it should not be forgotten that none of the compared image-based instruments had the capability to measure the size and shape of slender fibrillar fines (“crill”) or cellulose nanofibrils (CNF). Here, the qualitative and labour-intensive electron or atomic force microscopy methods remain the best options. Recent studies suggest that asymmetric flow field fractionation (A4F) and tunable resistive pulse sensing (TRPS) could be worthy further investigation (Laitinen and Niinimäki 2014; Weatherall and Willmott 2015).
7 References

L&W (2010): L&W FiberTester Operating Instructions, ABB Lorentzen & Wettre


Östlund, I., Personal communication to Hyll, K.: On the kappa number and SR of the UKSW Frövi pulp, Jul. 02, 2015.
8 Appendix – Detailed measurement results

8.1 Silica spheres results tables

<table>
<thead>
<tr>
<th>LD SiO2</th>
<th>20 ± 4 nm &amp; 80 ± 8 nm</th>
<th>350 ± 20 nm</th>
<th>2.06 ± 0.05µm</th>
<th>7.00 ± 0.29µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean SED [µm]</td>
<td>0.106</td>
<td>0.355</td>
<td>2.02</td>
<td>7.84</td>
</tr>
<tr>
<td>d10 [µm]</td>
<td>0.070</td>
<td>0.258</td>
<td>1.49</td>
<td>1.53</td>
</tr>
<tr>
<td>d50 [µm]</td>
<td>0.100</td>
<td>0.345</td>
<td>1.94</td>
<td>7.80</td>
</tr>
<tr>
<td>d90 [µm]</td>
<td>0.151</td>
<td>0.460</td>
<td>2.61</td>
<td>13.23</td>
</tr>
<tr>
<td>Span</td>
<td>0.810</td>
<td>0.586</td>
<td>0.58</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Table A 1. Volume-weighted results of MS measurements of silica spheres.

<table>
<thead>
<tr>
<th>350nm spheres</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of analysed particles</td>
<td>13082</td>
<td>17044</td>
<td>223</td>
<td>-</td>
</tr>
<tr>
<td>Area [µm²]</td>
<td>0.6 ±0.2</td>
<td>8.7 ±0.1</td>
<td>4.7 ±0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Perimeter [µm]</td>
<td>4.9 ±0.7</td>
<td>6.1 ±0.4</td>
<td>13.1 ±2.7</td>
<td>1.1</td>
</tr>
<tr>
<td>LRE [µm]</td>
<td>2.4 ±0.3</td>
<td>3.1 ±0.2</td>
<td>6.5 ±1.4</td>
<td>0.6</td>
</tr>
<tr>
<td>WRE [µm]</td>
<td>0.2 ±0.1</td>
<td>0.3 ±0.1</td>
<td>0.7 ±0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>ARRE</td>
<td>10.6 ±1.4</td>
<td>11.8 ±0.8</td>
<td>10.4 ±3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>LTR [µm]</td>
<td>0.9 ±0.1</td>
<td>1.1 ±0.2</td>
<td>2.7 ±0.7</td>
<td>See CED</td>
</tr>
<tr>
<td>WTR [µm]</td>
<td>0.8 ±0.2</td>
<td>0.8 ±0.1</td>
<td>2.0 ±0.7</td>
<td>See CED</td>
</tr>
<tr>
<td>ARTR</td>
<td>1.2 ±0.4</td>
<td>1.4 ±0.2</td>
<td>1.4 ±0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>CED [µm]</td>
<td>0.9 ±0.1</td>
<td>1.0 ±0.1</td>
<td>2.4 ±0.7</td>
<td>0.35 ±0.02</td>
</tr>
</tbody>
</table>

Table A 2. Mean and standard deviation of the mean of number-weighed parameters measured on the S350nm sample with IS60/40/20X.

<table>
<thead>
<tr>
<th>2µm spheres</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of analysed particles</td>
<td>8597</td>
<td>8299</td>
<td>7025</td>
<td>-</td>
</tr>
<tr>
<td>Area [µm²]</td>
<td>10.7 ±2.3</td>
<td>9.3 ±4.5</td>
<td>5.3 ±1.6</td>
<td>3.1</td>
</tr>
<tr>
<td>Perimeter [µm]</td>
<td>14.5 ±1.6</td>
<td>15.4 ±3.5</td>
<td>14.5 ±1.9</td>
<td>6.3</td>
</tr>
<tr>
<td>LRE [µm]</td>
<td>8.0 ±0.8</td>
<td>7.7 ±1.7</td>
<td>7.3 ±0.9</td>
<td>3.2</td>
</tr>
<tr>
<td>WRE [µm]</td>
<td>1.3 ±0.2</td>
<td>1.1 ±0.3</td>
<td>0.7 ±0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>ARRE</td>
<td>6.1 ±0.4</td>
<td>6.9 ±0.7</td>
<td>10.5 ±1.3</td>
<td>3.2</td>
</tr>
<tr>
<td>LTR [µm]</td>
<td>3.7 ±0.4</td>
<td>3.4 ±0.9</td>
<td>2.7 ±1.0</td>
<td>See CED</td>
</tr>
<tr>
<td>WTR [µm]</td>
<td>3.5 ±0.5</td>
<td>3.0 ±0.9</td>
<td>2.3 ±0.7</td>
<td>See CED</td>
</tr>
<tr>
<td>ARTR</td>
<td>1.2 ±0.1</td>
<td>1.1 ±0.2</td>
<td>1.1 ±0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>CED [µm]</td>
<td>2.6 ±0.4</td>
<td>3.3 ±0.8</td>
<td>3.7 ±0.4</td>
<td>2.06 ± 0.05</td>
</tr>
<tr>
<td>SED [µm]</td>
<td>3.8 ±0.7</td>
<td>3.9 ±0.9</td>
<td>2.7 ±0.4</td>
<td>See CED</td>
</tr>
</tbody>
</table>

Table A 3. Mean and standard deviation of the mean of number-weighed parameters measured on the S2µm sample with IS60/40/20X.
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Table A 4. Mean and standard deviation of the mean of number-weighed parameters measured on the S7µm sample with IS60/40/20X, FT+, and FT.

Table A 5. All instruments comparison. Volume-weighted mean sphere-equivalent diameter (SED), size range 0-9000 µm.

8.2 Fine fractions results tables

Table A 6. Volume-weighted results of MS measurements of model stocks, and the complex refractive index used in the evaluation of the data.
<table>
<thead>
<tr>
<th>Fines</th>
<th>Property (mean)</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
<th>FT+</th>
<th>FT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Analysed particles</td>
<td>12764</td>
<td>13209</td>
<td>1889</td>
<td>68989</td>
<td>36045</td>
</tr>
<tr>
<td></td>
<td>$L_{RE} [\mu m]$</td>
<td>11.3 ± 1.0</td>
<td>26.2 ± 9.2</td>
<td>56.6 ± 0.2</td>
<td>36.6 ± 2.2</td>
<td>34.3 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>$W_{RE} [\mu m]$</td>
<td>1.1 ± 0.1</td>
<td>2.7 ± 0.7</td>
<td>5.1 ± 1.5</td>
<td>11.8 ± 0.8</td>
<td>21.3 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>$AR_{RE}$</td>
<td>9.5 ± 0.3</td>
<td>10.5 ± 0.9</td>
<td>11.2 ± 1.8</td>
<td>4.1 ± 1.1</td>
<td>1.8 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>$L_{TR} [\mu m]$</td>
<td>6.9 ± 0.8</td>
<td>17.8 ± 9.8</td>
<td>35.8 ± 1.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$W_{TR} [\mu m]$</td>
<td>2.3 ± 0.1</td>
<td>4.6 ± 0.8</td>
<td>8.7 ± 0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$AR_{TR}$</td>
<td>2.6 ± 0.2</td>
<td>3.0 ± 0.8</td>
<td>3.6 ± 0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$CED [\mu m]$</td>
<td>3.9 ± 0.2</td>
<td>9.3 ± 2.6</td>
<td>18.7 ± 2.9</td>
<td>19.9 ± 0.1</td>
<td>28.0 ± 0.4</td>
</tr>
</tbody>
</table>

**Table A 7.** Fines measured by imaging instruments. Number of analysed particles (< 200 µm) and mean and standard deviation of the measured parameters. The values are area-weighted, and calculated from the subset of particles with length 0-200 µm.

<table>
<thead>
<tr>
<th>PCC</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
<th>FT+</th>
<th>FT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of analysed particles</td>
<td>174004</td>
<td>192179</td>
<td>199149</td>
<td>99997</td>
<td>60001</td>
</tr>
<tr>
<td>$L_{RE} [\mu m]$</td>
<td>8.0 ± 1.1</td>
<td>10.8 ± 0.6</td>
<td>9.8 ± 0.9</td>
<td>6.4 ± 1.0</td>
<td>33.2 ± 3.1</td>
</tr>
<tr>
<td>$W_{RE} [\mu m]$</td>
<td>1.2 ± 0.2</td>
<td>1.6 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>5.9 ± 0.1</td>
<td>20.9 ± 2.8</td>
</tr>
<tr>
<td>$AR_{RE}$</td>
<td>6.9 ± 0.1</td>
<td>7.4 ± 0.1</td>
<td>9.9 ± 0.2</td>
<td>1.2 ± 0.9</td>
<td>1.6 ± 0.6</td>
</tr>
<tr>
<td>$L_{TR} [\mu m]$</td>
<td>3.9 ± 0.6</td>
<td>5.2 ± 0.3</td>
<td>4.3 ± 0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$W_{TR} [\mu m]$</td>
<td>2.9 ± 0.3</td>
<td>4.0 ± 0.2</td>
<td>3.0 ± 0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$AR_{TR}$</td>
<td>1.2 ± 0.1</td>
<td>1.6 ± 0.1</td>
<td>1.1 ± 0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$CED [\mu m]$</td>
<td>3.5 ± 0.5</td>
<td>4.7 ± 0.3</td>
<td>3.7 ± 0.4</td>
<td>6.6 ± 0.2</td>
<td>27.6 ± 1.9</td>
</tr>
</tbody>
</table>

**Table A 8.** PCC measurements by the imaging instruments.
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<table>
<thead>
<tr>
<th>Mix</th>
<th>IS60X</th>
<th>IS40X</th>
<th>IS20X</th>
<th>FT+</th>
<th>FT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of analysed particles</td>
<td>20767</td>
<td>18957</td>
<td>19304</td>
<td>99997</td>
<td>60007</td>
</tr>
<tr>
<td>LRE [µm]</td>
<td>6.5 ± 0.4</td>
<td>10.6 ± 1.6</td>
<td>15.7 ± 1.4</td>
<td>19.5 ± 0.9</td>
<td>65.1 ± 2.0</td>
</tr>
<tr>
<td>WRE [µm]</td>
<td>0.9 ± 0.1</td>
<td>1.2 ± 0.3</td>
<td>1.3 ± 0.2</td>
<td>8.0 ± 0.1</td>
<td>25.1 ± 2.4</td>
</tr>
<tr>
<td>ARRE</td>
<td>7.5 ± 0.2</td>
<td>9.0 ± 0.2</td>
<td>11.5 ± 0.7</td>
<td>2.4 ± 0.1</td>
<td>3.5 ± 0.2</td>
</tr>
<tr>
<td>LTR [µm]</td>
<td>3.2 ± 0.5</td>
<td>5.6 ± 1.5</td>
<td>8.7 ± 4.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>WTR [µm]</td>
<td>2.2 ± 0.1</td>
<td>2.9 ± 0.3</td>
<td>3.3 ± 0.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ATR</td>
<td>1.4 ± 0.1</td>
<td>1.8 ± 0.2</td>
<td>2.0 ± 0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CED [µm]</td>
<td>2.6 ± 0.2</td>
<td>4.0 ± 0.9</td>
<td>5.0 ± 2.1</td>
<td>11.7 ± 0.2</td>
<td>40.1 ± 0.7</td>
</tr>
</tbody>
</table>

Table A 9. Mixture (UKSW fines and PCC) measurements by the imaging instruments.

<table>
<thead>
<tr>
<th>Mean SED</th>
<th>BKHW</th>
<th>TMP</th>
<th>UKSW</th>
<th>PCC</th>
<th>Mix (n 1.53)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT</td>
<td>34.4</td>
<td>40.1</td>
<td>48.4</td>
<td>46.4</td>
<td>39.3</td>
</tr>
<tr>
<td>FT+</td>
<td>21.4</td>
<td>36.4</td>
<td>24.4</td>
<td>7.9</td>
<td>21.5</td>
</tr>
<tr>
<td>IS20X</td>
<td>12.6</td>
<td>19.9</td>
<td>15.5</td>
<td>4.3</td>
<td>7.6</td>
</tr>
<tr>
<td>IS40X</td>
<td>9.7</td>
<td>15.5</td>
<td>7.7</td>
<td>5.7</td>
<td>5.0</td>
</tr>
<tr>
<td>IS60X</td>
<td>8.2</td>
<td>4.2</td>
<td>6.0</td>
<td>4.5</td>
<td>3.0</td>
</tr>
<tr>
<td>LD</td>
<td>49.9</td>
<td>48.0</td>
<td>56.4</td>
<td>4.4</td>
<td>47.7</td>
</tr>
</tbody>
</table>

Table A 10. All instruments comparison. Volume-weighted mean sphere-equivalent diameter (SED), size range 0-9000 µm.
9 Inventia Database information

Title
Optical methods for fines and filler size characterization – Evaluation and comparison

Author
Kari Hyll, Farnaz Farahani, Lars Mattsson

Abstract
The pulp fines and mineral fillers in the fine fraction of a papermaking stock influence process conditions and sheet properties. The influence is largely dependent on the size and shape of the particles. Quantitative characterization of the size and shape of fines and fillers would aid in process control and prediction of product properties. Thus, the aim of this study was to evaluate and compare optical instruments which can be used to quantitatively characterize the fine fraction of a papermaking stock. The compared instruments were the Mastersizer2000 from Malvern, based on diffraction scattering of a laser beam, the ImageStream from Amnis, and the L&W Fiber Tester and L&W Fiber Tester Plus from ABB Lorentzen & Wettre. The last three instruments are all based on imaging of the particles and have spatial resolutions ranging from 0.33 µm to about 10 µm per pixel.

All instruments overestimated the size of calibration spheres with known sizes. In several cases, calibration particles that were smaller than the spatial resolution of the instrument were detected. In these cases, the relative measurement error was large, likely due to positioning and quantization errors. It is also suggested that the oversizing was partly due to dissimilar optical properties of the calibration particles, compared to the typical sample, and that better calibration materials for fines need to be developed.

For the image-based instruments, the relative share of fines and filler particles increased as the size of the measured particles decreased. Thus, with higher spatial resolution, more particles were detected. However, the shape of the particle size distribution depended on the resolution and the field-of-view. The ImageStream resolved single PCC particles, which has not previously been done using flow microscopy. Due to its limited field-of-view, the ImageStream could not measure the largest fines, which were detected by the L&W Fiber Tester and L&W Fiber Tester Plus. While the L&W Fiber Tester Plus did not resolve single PCC particles, it detected, due to its higher resolution, a higher share of smaller particles than the L&W Fiber Tester. Overall, the ImageStream and the L&W Fiber Tester Plus were found to be complementary.

The diffraction-based method struggled to measure small fines. It is proposed that small fines diffract light insufficiently to be detected by the instrument. The obtained result was also highly sensitive to the choice of refractive index; a fact that some of the previous users apparently were not aware of.

In summary, image-based methods were found to perform better than the diffraction-based method when measuring on fines and mixtures of fines and fillers, while the highest resolution image-based instrument and the diffraction-based method were best when measuring on pure fillers.
Keywords
Stock, fine fraction, fines, fillers, size, shape, morphology, particle size distribution, particle characterization, flow microscopy, dynamic image analysis, laser diffraction, flow cytometry, PCC

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Insert classification

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