Preferred citation: S.M. Notley and L. Wågberg. Direct measurement of attractive van der Waals forces and repulsive electrostatic forces between regenerated cellulose surfaces in an aqueous environment. In Advances in Paper Science and Technology, *Trans. of the XIIIth Fund. Res. Symp. Cambridge, 2005,* (S.J. l'Anson, ed.), pp 1337–1350, FRC, Manchester, 2018. DOI: 10.15376/frc.2005.2.1337.

# DIRECT MEASUREMENT OF ATTRACTIVE VAN DER WAALS FORCES AND REPULSIVE ELECTROSTATIC FORCES BETWEEN REGENERATED CELLULOSE SURFACES IN AN AQUEOUS ENVIRONMENT

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## ABSTRACT

Using the colloidal probe technique, the interaction between carboxymethylated cellulose films and a cellulose sphere was studied. At low pH (pH 3.5), the interaction was dominated by dispersion forces. This was due to the low dissociation of carboxyl groups within the film at pH 3.5. However, at pH greater than 5, the interaction was dominated by an electrostatic repulsion. The increase in pH had the two-fold effect of completely dissociating the charged groups as well as causing appreciable swelling of the film leading to a decrease in the van der Waals component of the interaction. From these results it can be concluded that these cellulose films are suitable for a range of surface forces measurements including electrostatic, van der Waals', steric and adhesion

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forces. Furthermore, the measurement of forces using the colloidal probe technique can be extended to inorganic particles as well as for interactions between surfaces in the presence of for example wet and dry strength agents and other materials relevant to the paper-making industry.

## INTRODUCTION

The properties of wood- based materials and composites will be greatly influenced by the interaction forces between cellulose surfaces and between cellulose and other materials. Hence a fundamental understanding of the adhesion, friction and swelling properties of fibres in a material such as paper is dependant upon an understanding of the basic interactions between these cellulose surfaces. Furthermore, knowledge of the interactions between cellulose and many other materials relevant to the paper-making process such inorganic filler particles and polymeric additives used for retention and strength enhancing properties are of great fundamental importance and interest.

Typically, the potential energy of interaction between two surfaces as a function of surface separation is described using the somewhat simplistic Deryagin-Landau-Verwey-Overbeek (DLVO) theory[1, 2]. This theory assumes that the energy of interaction between two similar surfaces or particles is simply a sum of its attractive and repulsive components. The attractive component is comprised of dispersion forces while the repulsive component is due to the overlap of the electrical double layers.

Attractive forces have their origin in the induced dipole moment when two particles come into close contact whilst undergoing Brownian motion. These forces are known as van der Waals or dispersion forces[3]. The significance of the ubiquitous van der Waals attractive force on the strength and properties of the bonding between fibres in a paper sheet is still relatively unknown. The strength of the van der Waals interaction can be predicted if the system Hamaker constant (A) is known[4]. Bergstrom and co-workers have calculated the Hamaker constant for cellulose interacting across water to be  $8 \times 10^{-21}$  J from spectroscopic ellipsometry measurements[5]. The distance dependence (D) of the van der Waals interaction (E<sub>A</sub>) can be approximated by Equation (1) for a sphere interacting with a plane assuming no retardation effects are present.

Measurement of Attractive van der Waals and Repulsive Electrostatic Forces

$$E_A = \frac{-A}{6D^2} \tag{1}$$

The interaction between two charged surfaces as they come into contact will also be dependent upon the extent to which the local concentration of counter and co-ions exceeds that of the bulk. The overlap of the double layers will determine the electrical interaction potential. For similarly charged surfaces, the increase in the concentration of like charged ions in the intervening medium is unfavourable and will lead to a repulsive interaction potential. It is important therefore to understand what controls both the extension of the double layer from the surface and the magnitude of the ion build up close to the surface[3].

The distribution of both co-ions and counter-ions from a charged interface follows classical Boltzmann statistics. Thus, the electrical potential,  $\psi$ , as a function of distance, x, can be described, in the limit of low surface potential,  $\psi_0$ , by Equation (2).  $\kappa$  is the inverse Debye length and is often known as the thickness of the double layer. At low surface potentials, the potential decreases exponentially away from the surface. Apart from fundamental constants,  $\kappa$  depends only on the temperature, the charge on the ion and the bulk electrolyte concentration.

$$\psi = \psi_0 \exp(-\kappa x) \tag{2}$$

The potential energy of repulsion per unit area,  $E_R$ , can be obtained by calculating the work done in forcing the plates together against the opposing osmotic pressure between the two surfaces due to the accumulation of ions. Only the diffuse part of the double layer is considered in the calculation of the interaction as the full solution involves a complex tanh function that is difficult to solve analytically. For the interaction of two spheres, with equal radii r and small double layer overlap, the approximate solution given by Equation (3) holds where  $\varepsilon_0$  is the permittivity and D is the separation.

$$E_R = 2\pi r \,\varepsilon_0 \psi_0^2 \exp(-\kappa D) \tag{3}$$

Here we are talking about two spheres. It would be better to have a sphere on a flat or two flat surfaces considering what we have mentioned earlier and what will be mentioned later.

There have been a number of previous studies of the interaction forces present between cellulose surfaces. The first study, by Neumann et al[6], investigated the forces between regenerated cellulose films spun-cast onto

mica using the surface forces apparatus (SFA). The authors found a long range repulsive force, not purely electrostatic in origin and attributed this to cellulose chains "dangling" away from the interface. A subsequent SFA study by Holmberg et al investigated the interaction forces between regenerated celluloses surface prepared from trimethylsilyl cellulose deposited using the Langmuir-Blodgett technique[7]. Although AFM imaging showed these surfaces to be relatively smooth, a short range (at surface separations of less than 35 nm) steric interaction was omnipresent. Furthermore, no repulsive electrostatic force was observed with these surfaces indicating a complete lack of ionisable surface groups.

The development of the colloidal probe technique allowed the investigation of surface forces between far more varied substrates than previously possible with the SFA[8, 9]. Rutland and co-workers investigated the surface forces between porous cellulose spheres in aqueous salt solutions using this technique[10, 11]. Even though electrosteric repulsion was observed, at surface separations outside this regime the decay of the force could be satisfactorily fit to the electrostatic component of DLVO theory with the appropriate decay length predicted from the Debye length. Zauscher also found that electrostatics dominate the interaction between surfaces prepared from dialysis membranes made from regenerated cellulose and a cellulose sphere[12].

A number of new cellulose surface preparation methods have recently appeared in the literature[13–15]. Smooth, thin films have been prepared by spin-coating cellulose solutions on to silica wafers and then subsequent cellulose regeneration. The optimized method developed by Gunnars et al is of particular interest due to the ability of controlling the thickness and roughness of the films simply by choosing appropriate preparation conditions[13, 14].

Recent studies of the interaction forces using these newly developed cellulose thin films have shown great promise. Indeed, attractive van der Waals forces were observed under conditions where electrostatic interactions were minimized[16]. Thus these surfaces, in principle, can be used to investigate many different surface forces including electrostatic, steric, adhesion and friction forces.

In this study, the interactions between cellulose surfaces have been measured using an Atomic Force Microscope (AFM). Model cellulose surfaces with a high surface charge have been specifically prepared to mimic real wood-fibre systems. Both the van der Waals attraction and the electrostatic double-layer repulsion between the surfaces have been characterised.

## MATERIALS AND METHODS

## Materials

A dissolving grade pulp from Domsjö Fabriker, Sweden, was used as the raw material for the preparation of cellulose thin films. Glyoxolated polyacrylamide (G-PAM, Parez 631 NC) was used as the cationic anchoring polymer and supplied by Cytec, Germany. NMMO (N-methylmorpholine N-oxide) was supplied as a 50% w/w aqueous solution by Aldrich, Sweden while dimethyl sulfoxide (DMSO) was supplied by KeBo, Sweden. NaCl, HCl and NaOH were all of analytical grade and were used as supplied by Aldrich, Sweden. Milli-Q water was used in all experiments. Amorphous cellulose spheres, prepared from LiCl/dimethylacetamide solution, were provided by MonoGel AB, Helsingborg, Sweden.

Cellulose thin films were prepared according to a previously developed method[13, 14]. A cellulose solution was first prepared by dissolving 0.5g of pulp in 25g of NMMO at 115°C for approximately two hours. 75g of DMSO was then added to the solution in order to decrease the viscosity before spin-coating. Films were spin-coated at up to 3500 rpm for 30s onto oxidised silicon wafers pre-treated with an achoring layer G-PAM. This produced films with an approximate thickness of 30nm whilst minimising the surface roughness.

Bulk carboxymethylation was carried out on the dissolving pulp, according to the method of Walecka, in order to change the surface charge[17]. Pulps were prepared with a degree of substitution upto 0.09. The charge on the pulp was determined by conductometric titration against NaOH. It has been previously shown that the carboxyl groups are not removed during the dissolution process[18].

## Methods

## Surface roughness determination

Cellulose flat surfaces and spheres were imaged with Tapping Mode atomic force microscopy (Picoforce SPM, Veeco Inc., CA) to determine the surface roughness. These images were recorded in air with a TESP, rectangular silica cantilever (Veeco, Inc. USA). Roughness values were determined over a 1  $\mu$ m<sup>2</sup> image and are presented as root-mean-square (RMS) values.

## Colloidal probe microscopy

The interaction between a cellulose sphere and cellulose thin film was meas-

ured using colloidal probe microscopy. A Picoforce Scanning Probe Microscope (Veeco Ltd, Santa Barbara, CA) was used for all force experiments conducted in this study. Figure 1 shows a schematic diagram of the instrumental set-up. A cellulose sphere (of size between 5 and 20  $\mu$ m) was attached to the end of an AFM cantilever with a small amount of epoxy adhesive according to the method of Ducker et al[8, 19]. Standard, contact Si<sub>3</sub>N<sub>4</sub> cantilevers (Veeco, Santa Barbara, CA) were used for force measurements in this study. The data were typically collected using the 200  $\mu$ m long, thinlegged, triangular shaped cantilever with a spring constant of 0.095 N/m as measured by the thermal noise method[20].

Typically, the flat surface is ramped toward the sphere modified cantilever by the expansion of a piezoelectric scanner. Surface forces cause a measurable deflection of the cantilever. The deflection of the cantilever is converted to a force by Hookes' Law with the aid of the determined spring constant. The point of zero separation is defined as the onset of the constant compli-



Figure 1 Schematic representation of an atomic force microscope complete with colloidal probe attached. The deflection of the free end of the cantilever (where the colloidal particle has been attached) is measured as the fixed end of the cantilever spring is moved in a normal direction to the flat surface substrate.

ance region. That is, where a linear deflection of the cantilever is measured due to the linear motion of the flat substrate. This constant compliance region is also used to determine the optical sensitivity of the system. Once a pre-determined load is reached, the motion of the flat substrate is reversed and the adhesion between the surfaces can be measured. Zero force is defined as when the motion of the flat surface does not cause a measurable deflection of the cantilever. Both the forces on approach and retraction of the surfaces were measured, however, only the approach data will be discussed in this paper. At least 20 force-distance curves were measured and the data presented in this work are representative of the average of these curves.

Measured forces are normalized by the probe radius for comparison to theoretical fits of the surface force by the Derjaguin approximation[21]. The Derjaguin approximation relates the energy per unit area for two planar surfaces,  $E_{PP}$ , to the energy between a sphere and a flat plate by Equation (4), where FSP is the surface force and r is the radius of the sphere.

$$E_{PP} = \frac{1}{2\pi} \frac{F_{SP}}{r} \tag{4}$$

#### **RESULTS AND DISCUSSION**

#### Cellulose surfaces

Thin films of cellulose were prepared from dissolving grade pulp. This pulp was carboxymethylated to different degrees in order to probe the electrostatic component to the overall interaction force. Figure 2 shows an AFM Tapping Mode image of a highly charged cellulose flat surface (540  $\mu$ eq/g). Qualitatively, the morphology of all surfaces prepared as described above, regardless of charge, were similar, with rms roughness typically less than 2.0 nm over a 1  $\mu$ m<sup>2</sup> image.

The cellulose spheres were also imaged to determine their suitability for force measurements. Figure 3 shows an AFM Tapping Mode image of the interacting area of the cellulose sphere. The spheres were dried onto a glass slide prior to imaging. A large scan size is first used to determine the area of interest. Then, a much smaller scan,  $1 \ \mu m^2$ , was measured to determine the surface roughness. The rms roughess was 5.9 nm, far greater than for the flat surfaces. However, from geometric considerations, the rms roughness will be influenced by the natural curvature of the sphere.



**Figure 2** AFM tapping mode images in air of a highly charged (540  $\mu$ eq/g) cellulose thin film. Height image (1  $\mu$ m<sup>2</sup>, z range for the surface is 10 nm). The surface roughness, expressed as an rms roughness over 1  $\mu$ m<sup>2</sup>, was 1.9 nm. Left image is 10  $\mu$ m<sup>2</sup> and right image is 1  $\mu$ m<sup>2</sup>.



**Figure 3** AFM image of the interacting area of the cellulose sphere. Height image  $(1 \ \mu m^2, z \ ranges$  for the sphere is 50 nm) was obtained using tapping mode. The surface roughness (RMS) over a  $1 \ \mu m^2$  image of the interacting area of the sphere was 5.9 nm. The radius of the cellulose sphere was 13.5  $\mu m$ .

#### Attractive van der Waals forces

In a previous study, attractive van der Waals' forces were observed using similar, non-carboxymethylated surfaces. Here, the attractive forces are probed using charged surfaces. Figure 4 shows a representative force-distance curve for the interaction of a 540  $\mu$ eq/g charged surface and sphere across an aqueous NaCl solution. The solution pH was 3.5. At this pH almost all ionisable groups in the cellulose films should be associated and as such, the cellulose film should be virtually uncharged.

As can be seen from Figure 4, the long range attraction can be well fitted using Equation (1) with a Hamaker constant of  $9 \times 10^{-21}$  J. A slight electrostatic repulsion can be observed in Figure 4 due to the dissociation of some carboxyl groups in the cellulose film. However, this electrostatic component is barely noticeable above the background noise levels.

#### Electrostatic interactions

The dissolving pulp was carboxymethylated prior to dissolution in order to vary the surface charge of the spin-coated cellulose films. Thus, by choosing



#### apparent separation (nm)

**Figure 4** Interaction between a cellulose sphere (radius 13.5 µm) and flat cellulose surface (540 µeq/g charge) in an aqueous NaCl solution (1 mM) at pH 3.5. The solid line is a fit to the nonretarded Hamaker equation (Equation (1)) with a Hamaker constant of  $9 \times 10^{-21}$  J.

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appropriate solution conditions, it was possible to investigate the electrostatic repulsion between the charged surfaces as a function of pH and ionic strength. Figure 5 shows the normalised force curves as a function of ionic strength for a 540 µeq charged cellulose film interacting with an unmodified sphere. As can be seen from Figure 5, the force exponentially decays with distance indicating that the surfaces behave according to DLVO theory. The change of the fitted decay with a change in salt concentration excellently agrees with the change in the Debye screening length for the ionic strengths indicated. The measured Debye lengths were 30 nm and 95 nm for 0.1mM and 0.01mM respectively.



Figure 5 Interaction between a cellulose sphere (radius  $13.5\mu$ m) and flat cellulose surface (charge of 540 µeq) in aqueous NaCl solutions at pH 8.5. NaCl solution concentrations, 0.1mM (closed symbols) and 0.01mM (open symbols). The forces decay exponentially with distance indicating a good agreement with the electrostatic interactions as described by the DLVO theory. The measured Debye lengths were 30 nm and 95 nm for 0.1mM and 0.01mM respectively. The scatter in the data at low force is due to thermal noise.

#### Influence of swelling

The force-distance curves in Figures 4 and 5 demonstrate the utility of using well defined cellulose model films. By simply tuning the solution pH, conditions were created that favoured either van der Waals' attractive forces or electrostatic repulsive forces. Whilst dispersion forces are ubiquitous and generally unaffected by varying aqueous solution conditions, that is, they are always present and more or less constant (see Equation (1)), they are insignificant to the overall interaction potential, until very small surface separations, when dealing with highly charged surfaces such as those found for these cellulose films at pH > 5.

Furthermore, when determining the magnitude of the van der Waals's interaction between cellulose surfaces, the effect of swelling must be considered. The Hamaker constant is used to give a relative measure of the strength of the dispersion forces present in the system. However, the Hamaker constant only provides information for the case in the absence of swelling, that is, pure cellulose interacting across water. If the films are appreciably swollen with water, the effective concentration of cellulose in the film decreases. Thus, the overall attractive energy in the force interaction will also decrease.

Figure 6 shows a comparison of force-distance profiles between the highly charged cellulose surfaces interacting in an aqueous NaCl as a function of pH. At low pH, virtually no carboxyl groups are undissociated leading to a minimal surface charge. Therefore, in the absence of any substantial electrostatic contribution to the overall interaction force, and perhaps more importantly, any high swelling forces due to the charges located throughout the film, the van der Waals' attraction dominates.

As the carboxyl groups become undissociated with increasing solution pH, the cellulose film tends to swell[14]. Thus, the van der Waals' component will diminish at the same time as the development of a significant electrostatic barrier. Thus the electrostatic component dominates with no observable jump into contact between the two surfaces due to dispersion forces.

#### Importance of surface forces in paper-making

As already mentioned, a number of different types of surface forces are everpresent in cellulose systems. The most obvious are, of course, the ubiquitous van der Waals interactions and forces due to the charged nature of the fibres. It will be this delicate interplay between attractive and repulsive forces which determines the way in which wood-based fibres come together to form joints in a paper-sheet[22]. Thus, the relative magnitude of these DLVO type forces



**Figure 6** Comparison of force profiles between highly charged cellulose surfaces (540 µeq/g) as a function of pH in a 1mM NaCl solution. Closed symbols, pH 8.5 and open symbols, pH 3.5.

will highly influence the adhesion between fibres and hence the strength of paper.

Furthermore, with the increasing use of recycled fibres and inorganic filler particles, it is of fundamental importance to understand the forces of interaction between a range of cellulose and other materials, not just between cellulose surfaces. This quantified knowledge is vital if the decrease in strength properties of paper made with these constituents is to be addressed.

The influence of polymeric additives on the interaction between cellulose is also of high interest. These non-DLVO type forces are also well known to influence stability and adhesion. Thus, the colloidal probe technique can easily be adapted to probe interactions between surfaces in the presence of wet and dry strengthening agents.

#### CONCLUSIONS

Cellulose films were prepared from carboxymethylated dissolving pulp and the interactions between cellulose surfaces in aqueous conditions have been determined. Forces due to van der Waals' interactions and electrostatics have been measured using colloidal probe microscopy. At low solution pH, a long range van der Waals' attraction dominated the interaction. However, at high pH, that is, at pH above the pKa of the carboxyl groups in the film, electrostatics dominated the interaction. Excellent agreement with DLVO theory was found for both the van der Waals dominated case as well as the electrostatic dominated case. The excellent stability of these films, even when subjected to high swelling forces, means these surfaces are ideally suited to measurements of a range of surface forces.

#### ACKNOWLEDGMENTS

S.N. would like to acknowledge financial support from the BioFibre Materials Centre, KTH, and the Bo Rydin Foundation. The Stiftelsen Nils and Dorthi Troëdssons Forskningsfond is gratefully acknowledged for the provision of the Atomic Force Microscope.

## REFERENCES

- 1. Deryagin, B., Landau, L., Acta. Phys. Chim. U. R. S. S., 1941. 14: p. 633-662.
- 2. Verwey, E.G.W., Overbeek, J. T. G., *Theory of the stability of lyophobic colloids*. 1948, New York: Elsevier.
- 3. Israelachvili, J., *Intermolecular and surface forces*. 2nd Edition ed. 1991: Academic Press.
- 4. Hamaker, H.C., Physica, 1937. 4: p. 1058.
- 5. Bergström, L., et al., Cellulose, 1999. 6: p. 1-13.
- 6. Neumann, R.D., J.M. Berg, and P.M. Claesson, Nordic Pulp Paper Res. J., 1993. 8: p. 96–104.
- Holmberg, M., Berg, J., Stemme, S., Odberg, L., Rasmusson, J., Claesson, P., Surface force studies of langmuir-blodgett cellulose films. J. Colloid Interface Sci., 1997. 186: p. 369–381.
- 8. Ducker, W.A., Senden, T. J., Pashley, R. M., Nature, 1991. 353: p. 239.
- 9. Butt, H.-J., Biophys. J., 1991. 60: p. 1438.
- 10. Rutland, M.W., et al., Colloid Surf. A, 1997. 123-124: p. 369-374.
- 11. Carambassis, A., Rutland, M., Interactions on Cellulose surfaces: Effect of electrolyte. Langmuir, 1999. 15: p. 5584–5590.
- 12. Zauscher, S., Klingenberg, D. J., Normal forces between cellulose surfaces measured with colloidal probe microscopy. J. Colloid Interface Sci., 2000. 229: p. 497–510.
- 13. Gunnars, S., L. Wågberg, and M.A. Cohen-Stuart, Cellulose, 2002. 9: p. 239-249.
- 14. Fält, S., L. Wågberg, and E.L. Vesterlind, Swelling of Model Films of Cellulose

Having Different Charge Densities and Comparison to the Swelling Behavior of Corresponding Fibers. Langmuir, 2003. 19: p. 7895–7903.

- 15. Kontturi, E., P.C. Thune, and J.W. Niemantsverdiet, *Novel method for preparing cellulose model surfaces by spin coating*. Polymer, 2003. 44: p. 3621–3625.
- Notley, S.M., B. Petterson, and L. Wågberg, Direct Measurement of Attractive van der Waals' Forces between Regenerated Cellulose Surfaces in an Aqueous Environment. J. Am. Chem. Soc., 2004. 126: p. 1393013931.
- 17. Walecka, J.A., An investigation of low degree of substitution carboxymethylcelluloses. TAPPI J., 1956. 39: p. 458–463.
- 18. Fält, S., *Model Studies of cellulose fibers and films and their relationship to paper strength.* 2003, KTH: Stockholm.
- 19. Ducker, W.A., Senden, T. J., Pashley, R. M., Measurement of forces in liquids using a force microscope. Langmuir, 1992. 8: p. 1831–1836.
- Hutter, J.L., Bechhoefer, J., Calibration of atomic force microscope tips. Rev. Sci. Instrum., 1993. 64: p. 1868–1873.
- 21. Derjaguin, B.V., Kolloid Z., 1934. 69: p. 155.
- 22. Torgnysdotter, A. and Wågberg, L., Nordic Pulp Paper Res. J. 2004. 19: p. 440-447

## **Transcription of Discussion**

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Theo van de Ven McGill University

Nice data. I wonder about the charge of your cellulose surfaces. You mentioned a number of 320  $\mu eq/g$ . How does this translate into charge per unit area? Can you calculate the zeta potential or surface potential using the Gouy-Chapman theory from this? How would that compare to the potentials you have found from the force measurements?

#### Lars Wågberg

We have not done that. It is a good suggestion and I would definitely assume that you will come up with a higher value then we estimated from our experiments. Thank you for the comment.

#### Discussion

#### Vladimir Grigoriev Nalco

I'm quite impressed with your work. From my personal experience with cellulose probes I can say that the colloid probe technique is not easy to use. One problem that I encountered was swelling of the cellulose spheres in water. In your calculations you used measured forces normalized by the probe radius, which would change in water due to swelling. How did you handle this complication?

#### Lars Wågberg

What we did was that we checked how these spheres changed as they were exposed to water. If I remember correctly they do not swell much and the radius we used in the calculation is the wet radius. When I say it is porous, I mean somewhat porous. It is not to be compared with the cellulose beads you can buy commercially. The product we have been using is of course a commercial product but the company that supplied the sample is very small and they have just started to sell this product. It is a much less porous material compared to other available materials. It is a bit rough, but it is much, much better when it comes to porosity.

#### Vladimir Grigoriev

Perhaps I was using cellulose spheres that were more prone to swelling.

#### Lars Wågberg

I guess you were.

#### Vladimir Grigoriev

Are the cellulose spheres you used commercially available?

#### Lars Wågberg

Yes. I do not know the full range of commercially available fractions but the fraction, the tiny fraction, that we have received was a special delivery to us. However, if it was a special delivery to us it could be a special delivery to you as well.

#### Bob Pelton

The initial film you showed us gave pure DLVO behaviour. Then you showed us the structural changes when you get these fibril surfaces. Do they still follow DLVO behaviour? What will the force curve look like for the heat-treated films?

#### Lars Wågberg

I do not recall any data on that, but on the other hand, the surfaces still have a very low surface roughness so I assume the measurements would still be pretty good.