Raman microscopy in lateral mapping of chemical and physical composition of paper coating

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ABSTRACT: This paper shows how confocal Raman microscopy reveals the distribution of paper coating chemicals in the x-y plane. The use of two microscope objectives enabled bulk and surface analysis of styrene butadiene (SB) latex and calcium carbonate in coated papers. In the bulk coating analysis, spatial mapping of chemical distribution covered 0.15 mm^2 areas with a 10 µm lateral resolution. We analyzed a 1 mm^2 area in shorter measurement time by using a coarser lateral resolution. The bulk compositional maps revealed the distribution of chemicals and gave information on the coating thickness. These measurements were possible to perform through magenta ink; information about ink density could be obtained at the same time. In the surface analysis, the analyzed layer was only about 2 µm thick. The surface measurements were obtained from a larger area (26 cm^2), but using fewer measurement points. That led to a shortened analysis time, while giving even more valid quantitative results on the variation of SB-latex content.

Application: Lateral Raman mapping can be used to analyze bulk and surface latex distribution. Moreover, bulk mapping gives information about coating thickness and ink density variations.

Pigmented coatings are commonly used in the paper industry. These coatings not only increase the brightness and opacity of the final product, but also serve as good printing substrates. The properties of the coating surface determine the quality of final print. Some optical and printing defects may be linked to a nonuniform composition of coating layers [1, 2]. Therefore, it is important to have methods for characterizing the coating surface and monitor the quality.

Many methods are available for chemical characterization of paper coating surfaces. For example, laser induced plasma spectroscopy [3], IR-spectroscopy [4], secondary ion mass spectrometry [5] and Raman microscopy [6, 7] have been used in the mapping of paper coatings in lateral directions. (Groves *et al.* compared the different analytical methods and evaluated their suitability for print mottling characterization [8].)

Raman microscopy has some advantages over the other techniques. Most of the samples can be measured without further preparation. Raman is a nondestructive method. The achieved spatial resolution is close to 1 micrometer, a length scale that is smaller than in many other methods. Moreover, in Raman microscopy, it is simple to change spatial resolution by changing objectives. The biggest difficulties in Raman technique usually come from fluorescence. Kaolin based paper coatings are prone to fluorescence.

Raman microscopy has been used quite extensively for lateral mapping in various areas, including pharmaceuticals, living cells, polymeric materials, and diamond-like coatings [9-12]. Raman microscopy, as an analytical tool for coated paper is still new, but the number of reports on its use is increasing. The older Raman studies focused on the identification of the constituents of old manuscripts, paintings, and artwork or on the determination of amounts of pigments in recycled paper [13, 14]. A Raman microscope system was used to study print mottling [15]. In that study, mottling was more related to the variations in coating thickness than to uneven latex distribution in the coating layer. In this case, the coating heterogeneity and mottling were determined from microscopic cross-section analysis, and Raman microscopy was used only for SB-latex quantification.

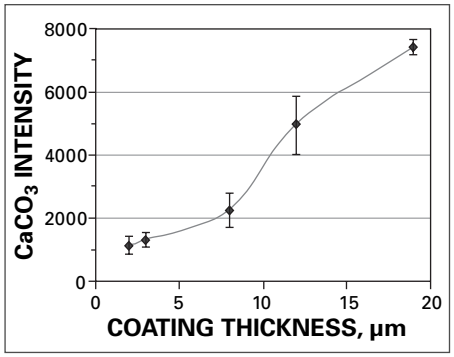
Recently, several studies used confocal Raman microscopy to analyze binder migration in paper coatings [6, 16, 17]. The researchers were able to observe migration of coating components in the depth direction of coating using microtome cutting, direct confocal Raman depth profiling, or by monitoring the surface concentration. However, in these papers, the migration was studied within a limited area. Analysis of larger areas would be more interesting because human vision cannot see small details. In our previous preliminary work, we considered larger area mapping of bulk coating layer [7]. Because the same system is used in this work, the earlier findings of bulk coating analysis can be used directly.

This work concentrates on paper coating analysis in the x-y plane using confocal Raman microscopy. The same information may be extracted from confocal Raman depth profiles, but enormous time savings are gained by direct studies of lateral distributions. In lateral mapping, the measurement areas can be easily increased to cover areas that are larger than printing defects. This work can be divided into two separate parts: analysis of the bulk coating layer and analysis of the coating surface. We altered the analysis depth by changing the microscope objective from 10X to 100X. For the surface analysis, we developed a new measurement scheme. By means of the new scheme, quantitative measurement of both small- and large-scale variation of binder is obtained.

MATERIALS AND METHODS

Samples

Sample set 1—The effect of coating thickness on Raman intensity was studied using coatings spread with a laboratory slit rod coater on a glossy polyethylene



1. Measured Raman intensity of calcium carbonate for different coating thicknesses. Error bars are given as 95% confidence interval.

terephtalate (PET) substrate. Analyzed average thicknesses were 1.5, 2.5, 7.5, 11.5, and 19 µm. These coatings contained 100 parts per hundred pigment (pph) of calcium carbonate ($CaCO_3$; Omya, Hydrocarb 90) and 12 pph of SB-latex (Dow, DLL 966).

Sample 2—A printed paper sample was used to illustrate a good resolution spatial mapping. A calcium carbonate containing fine paper was coated on a pilot coater at 800 m/min at KCL, Espoo, Finland. The coating color contained 50 pph of calcium carbonate (Omya, Hydrocarb 90), 50 pph of kaolin (Huber, Hydragloss 90), 15 pph of SB-latex (Dow, DLL 966), and 0.7 pph of carboxymethylcellulose (CMC) (Noviant, Finnfix 10). The solids content of the coating color was 65% and the target coat weight was 12 g/m^2. The coated paper was calendered and printed in a four-color, sheet-fed offset press at KCL, Espoo, Finland.

Sample 3—A lateral map was measured from a printed paper sample with 100% magenta ink coverage. A calcium carbonate containing fine paper was coated on a pilot coater at 800 m/ min at KCL. The coating color contained 100 pph of calcium carbonate (Omya, Hydrocarb 90), 15 pph of SB-latex (Dow, DLL 966), and 0.7 pph of carboxymethylcellulose (CMC) (Noviant, Finnfix 10). The solids content of the coating color was 65% and the target coat weight was 12 g/m^2. This coated paper sample was printed in a four-color, sheet-fed offset press at KCL.

Sample 4—Surface analysis of coated paper was performed using a sample that was coated at KCL. The coating contained 100 pph of calcium carbonate (Omya, Setacarb), 11 pph of SB-latex (Dow, DL940), and small amounts of optical brighteners, starch, and CMC. The target coat weight was 12 g/m^2.

Sample 5—This sample was also used in the surface analysis. Sample 4 was otherwise similar to the Sample 3, but the calcium carbonate pigment size was larger (Omya, Hydrocarb 60).

Confocal Raman microscopy

Raman spectra were collected with a dispersive Kaiser Optical Systems HoloLab Raman instrument equipped with a 785 nm wavelength diode laser and an Olympus BX 60 microscope. The laser power at the sample stage was 35 mW. For the bulk coating mapping, we used a metallurgical 10X (NA 0.25) objective. The lateral resolution with this objective was about 10 µm and the analysis depth was about 10-15 µm when analyzing light scattering paper coatings. For surface-sensitive measurements, we used a metallurgical 100X (NA 0.95) objective featuring about a 2 µm measurement spot and an analysis depth of about 1-2 µm. For automatic mapping, the system had a motorized x-y stage (Coherent EncoderDriver, 37-0486) and an objective scanner for the movement in z-direction (Physik Instrumente's PIFOC, P-721.10).

Automatic focusing software was programmed to ensure good collection efficiency in the whole area. The focusing was performed in two stages: coarse focusing first, in 5 µm steps, then fine focusing in 1 µm steps. Measurement time for these successive focusing measurements was 1 s. We used the band height of calcium carbonate at 1084 cm^{-1} to find the focal position.

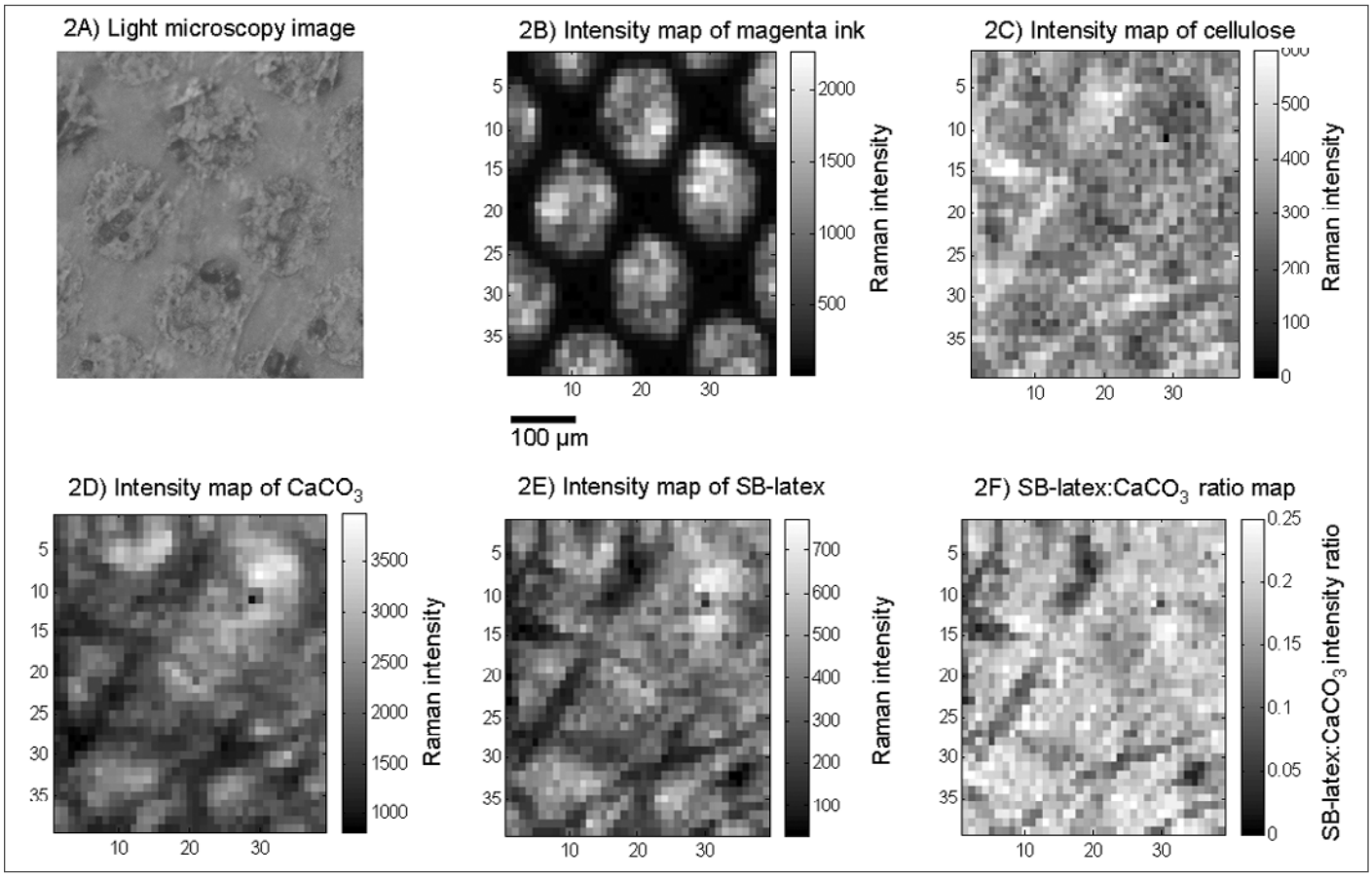
RESULTS

Sample set 1 was used to illustrate the effect of coating thickness on calcium carbonate intensity. **Figure 1** shows that by using a 10X objective in a HoloLab Raman microscope, the analyzed intensity changed markedly when the thickness was around 10 µm. Light scattering properties of the coating may vary with different coatings, causing changes in the Raman intensity. Consequently, the curve shown in Figure 1 cannot be used as a general calibration curve. Error in the coating thickness is marked in the thinnest coatings. The use of pure Raman intensities without normalization also causes errors. Although the method does not provide quantitative information about coating thickness, it demonstrates that the variation in Raman intensity comes from the variation in coating thickness. We found in our earlier work [7] that with a 10X objective, the change in the intensity due to defocusing is small. The intensity was quite constant on a broad focusing range covering approximately 60 µm in the z-direction.

Spatial mapping of paper coating

A good resolution Raman map was measured from a printed area of sample 2. The area of the measurement was 390 µm x 390 µm. The step size between the successive measurement points was 10 µm. The total number of Raman spectra was 1521. The analysis time was about 9 hours. **Figure 2A** shows a light microscopy image of the same area of magenta print where the Raman map was measured. From the Raman spectra it is possible to obtain a separate image for each component that is visible in the spectra. **Figures 2B-E** show pure Raman intensity maps of selected components. Quite similar features are observed in calcium carbonate and in the SB-latex intensity maps (Figs. 2D-E). Clearly, these images show a similar pattern as seen in Fig. 2C, which shows the cellulose intensity in that area. These results indicate that a thinner coating layer occurs in the areas where cellulose fibers are closer to the surface. For quantitative analysis of SB-latex, its intensity ratio to calcium carbonate can be used. For unknown samples, relative variations can be quantified due to the linear response of Raman spectroscopy. **Figure 2F** indicates that thinner coating areas have less SB-latex relative to calcium carbonate. The calcium carbonate filler in the base paper may change the observed ratio. Otherwise, this may indicate that base paper has filtered the larger calcium carbonate pigments while permeating part of the smaller latex particles into the base paper.

Figure 3 presents Raman maps and a light microscopy image of sample 3. The area of the measurement was 1.16 mm x 0.92 mm. The step size between the successive measurement points was 40 µm. The total number of Raman spectra was 720. The analysis time was

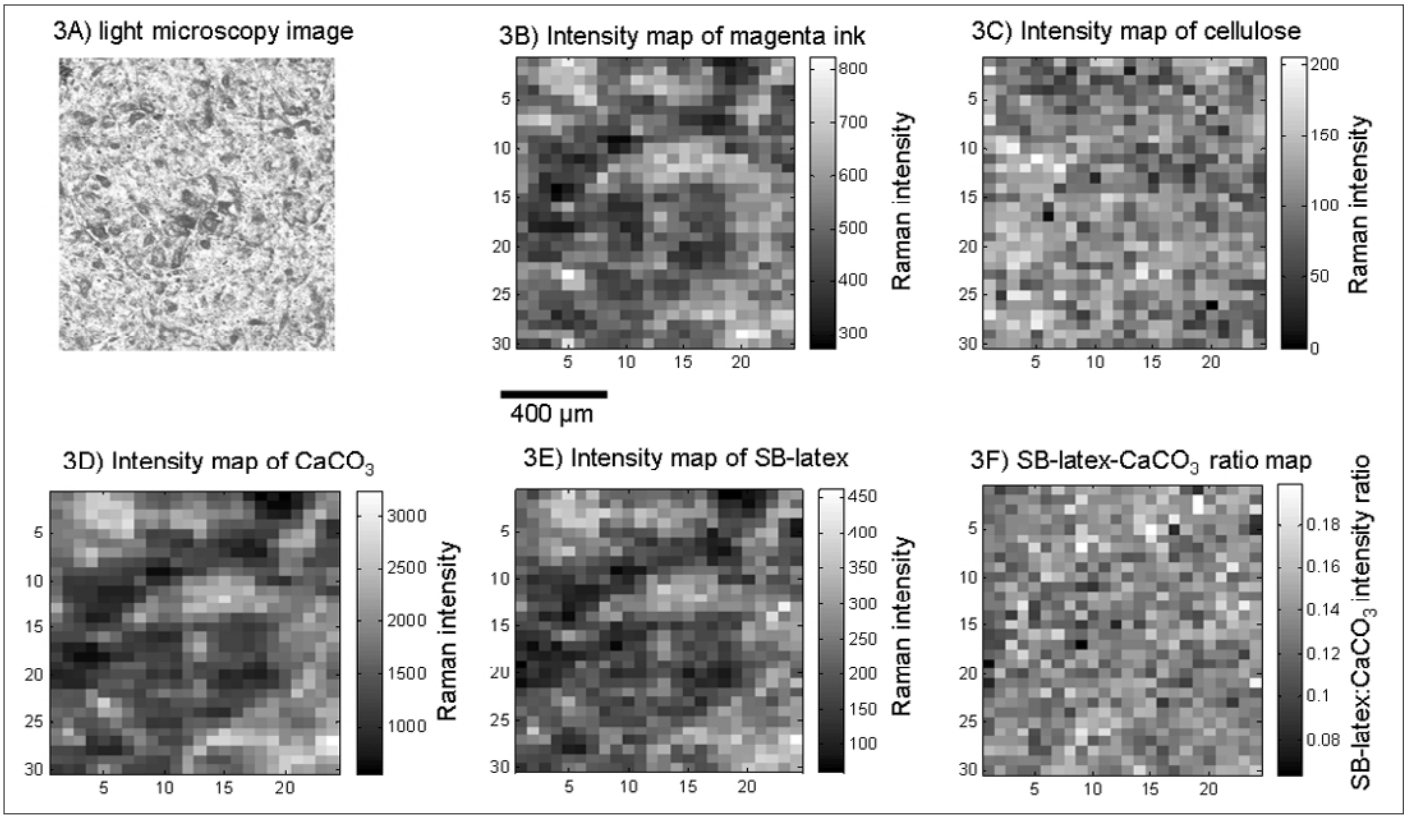


2. Raman maps of sample 2 from an area 390 µm x 390 µm. The step size was 10 µm in the x-y direction. Light microscopy image A is from the same area as Raman maps B-F. Raman maps show the pure Raman intensities of the selected components and the SB-latex:$CaCO_3$ ratio map show the intensity ratio.

approximately 4.5 hours. During collection of the spectrum, we moved the sample under the laser beam in a controlled way to increase the effective measurement area to 40 µm^2. Automatic focusing was performed before each Raman spectrum acquisition to compensate for the sample roughness. Again, calcium carbonate and SB-latex (Fig 3D-E) exhibit wide, but similar, variation in intensity. Cellulose (Fig. 3C) shows higher intensities in areas where the coating intensities were lower, indicating variation in coat weight. A large variation is also observed in the magenta ink pigment intensity map (Fig. 3B) and "holes" can be observed in the light microscopy image (Fig. 3A) of low ink density areas. By comparing the ink intensity map and the SB-latex distribution, given in the SB-latex:$CaCO_3$ map (Fig. 3F), it can be seen that the correlation between the ink density and SB-latex distribution is not as strong as it is between the ink density and coat weight. As is evident from Figure 3F, the SB-latex distribution is somewhat even, though variations can be seen in areas of low coat weight, mostly due to noise appearing at low Raman intensities. The mean SB-latex:$CaCO_3$ ratio (x100) was 13.5 and the relative standard deviation was 14.0%. This sample shows that the SB-latex distribution is somewhat uniform and does not correlate to ink density variations, but variation in the coat weight does relate to ink density variation.

Surface analysis of paper coating

Spatial resolution in the x-y plane can be decreased by moving the sample during the acquisition of a Raman spectrum. We used a sinusoidal movement curve that covers an area of 150 µm x 150 µm. The sample was set to travel several times back and forth giving an average Raman spectrum from the whole 150 µm x 150 µm area. Moreover, the shallow analysis depth of the 100X objective was maintained. Automatic focusing was performed at each measurement point before the sample movement was started. A video camera attached to the microscope allowed us to follow the laser spot during the scanning. We observed small changes in focus resulting from paper surface roughness, regardless of automatic focusing performed in the beginning of the scanning. However, these changes were generally small and the change in focus does not have any effect on quantification because we used a latex:pigment ratio. **Figure 4** shows the measurement scheme for paper coating surface analysis. To get good mean and standard deviation values within a 1 mm x 1 mm area, we measured 25 Raman spectra. Bigger steps were then taken between the 1 mm x 1 mm areas to cover larger areas of sheet.



3. Raman map from a 1.16 mm x 0.92 mm area of sample 3. The step size was 40 µm in the x-y direction. Raman maps B-E show Raman intensities of the selected components and the Raman map F show SB-latex distribution, which is given as the SB-latex:$CaCO_3$ intensity ratio.

We used sample 4 to test the repeatability of the instrument. We repeated 10 measurements at the same position. This test gave a single measurement uncertainty for the instrument. The coefficient of variation was 2.8% for the SB-latex:$CaCO_3$ ratio. By doing multiple measurements, averaging leads to a smaller standard error, which is inversely proportional to the square root of the number of measurements.

The surface analysis was performed for samples 4 and 5. We analyzed 10 sheets according to the measurement scheme illustrated in Fig. 4. It is clear that this kind of coarse map does not give detailed spatial information. To obtain valid quantitative results on the magnitude of larger scale variation, however, it is better to artificially expand the measurement spot and spread the points across the sheet, preferably over several sheets. Analysis time for a single 1 mm x 1 mm area containing 25 spectra was approximately 20 min. Standard deviation of the 25 SB-latex:$CaCO_3$ ratios in the 1 mm x 1 mm area was used to indicate the magnitude of small scale latex variation. Larger area variation was determined by calculating the mean latex:pigment ratios in each 1 mm x 1 mm area. Standard deviation of these mean latex:pigment ratios was used as a measure of the magnitude of large scale latex variation. Using this method, it was possible to get separate statistical values for the two different length scale variations.

The data in **Table I** show that the two different pigment systems had unequal variations in the latex content. The observed mean intensity ratios also differed because of the different pigment types. The number of the 1 mm x 1 mm areas and sheets were decreased to see if less measurement would give similar results (black areas in Fig. 4). The 95% confidence intervals show the change in the accuracy of SB-latex quantification when decreasing the number of measurements. Three 1 mm x 1 mm areas measured from three sheets seem to be enough for these samples to quantify SB-latex quite well. However, large area variation can be more sensitive for the sample composition and measurement position, because only nine mean values are used to determine the large area variation in the three-sheet case.

CONCLUSIONS

Raman microscopy provides an easy way to determine relative variations in SB-latex content without calibration. Raman measurements can be performed at different probing depths, giving information about bulk coating, including its thickness, or coating surface. In principle, these two type of lateral mapping measurement could be taken from the same area, thus also providing an idea about binder migration. Latex content variation on different length scales also can be studied by averaging measurements. The capability to do the measurement through certain printing inks may yield new information about printing defects, especially if it is possible to relate printing defects to distributions of

coating chemicals or physical structure of a paper coating. Bulk mapping of paper coating can be used to study ink density, coating thickness and SB-latex distribution at the same time. The capability to characterize coating surfaces also is important because the interaction between a coating and an ink takes place within the top few micrometers of the paper surface. **TJ**

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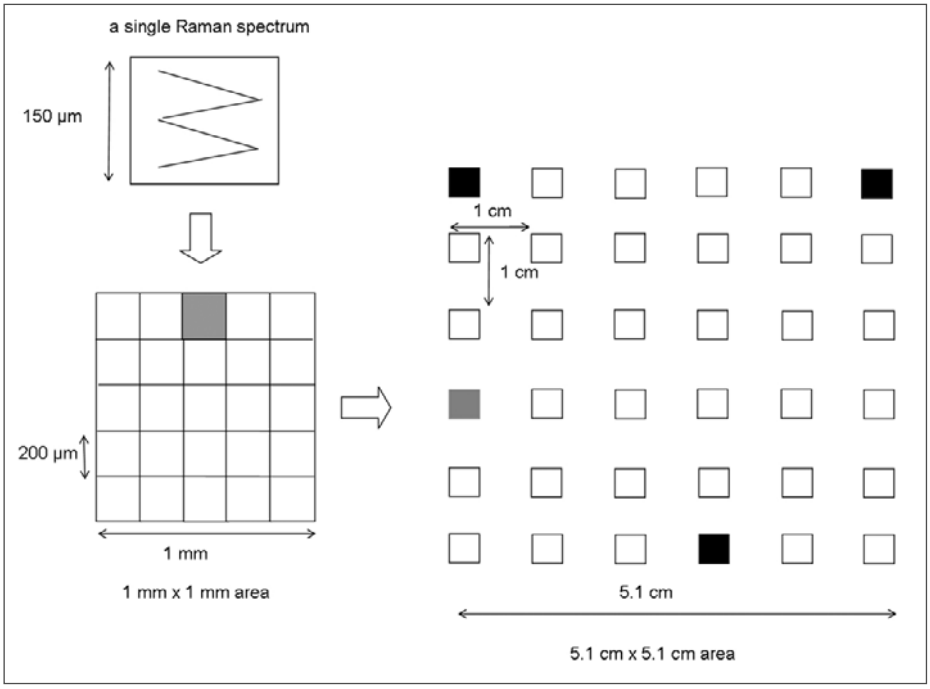

4. Measurement scheme for the surface analysis. Average Raman spectra were measured from each area of 150 µm x 150 µm by moving the sample during the measurement. By using a step size of 200 µm, a measurement matrix of 5 x 5 covered an area of 1 mm x 1 mm. Black areas represent the measured areas when only three 1 mm x 1 mm areas were measured.

	36 areas of 1 mm x 1 mm 10 sheets	3 areas of 1 mm x 1 mm 3 sheets
Mean of SB-latex: $CaCO_3$ ratio x 100 Sample 4 / 5	9.5 / 13.0	9.6 / 13.2
95 % confidence interval for mean Sample 4 / 5	0.02 / 0.02	0.13 / 0.12
SB-latex variation in 150 µm x 150 µm area, % Sample 4 / 5	9.8 / 6.5	10.2 / 6.9
SB-latex variation in 1 mm x 1 mm area, % Sample 4 / 5	5.1 / 1.9	4.5 / 1.6

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INSIGHTS FROM THE AUTHORS

Many earlier studies have suggested that uneven latex content causes print mottle. Raman spectroscopy provides a means to analyze latex content and its distribution. However, the technique has not yet been used extensively in paper coating analyses, or the analysis areas have been small compared to that of mottling scale. This same confocal Raman microscope has also been used for depth profiling of coated papers.

One difficult aspect of this work was to increase the area of the surface Raman measurement to mottling scale, especially when measuring rough paper samples. We overcame that by programming an averaging sample movement and automatic focusing.

The principle aim of this study was to measure latex content and its distribution. During the work, however, we found that bulk coating maps also reveal coat weight and ink density variation. Hence, latex content variation could be compared to coat weight and ink density variation.

The paper industry may find Raman microscopy useful for quality control, product development, and research purposes for latex content or distribution analysis. As a non-contact method, Raman may also be applied to on-line analysis.

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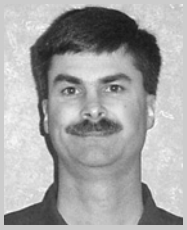
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