Confocal Raman microscopy in the analysis of coated and printed papers

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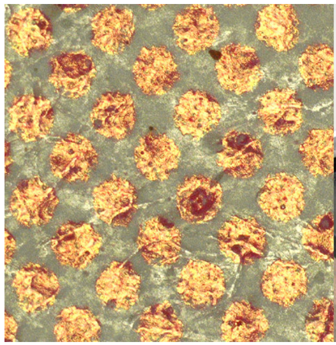
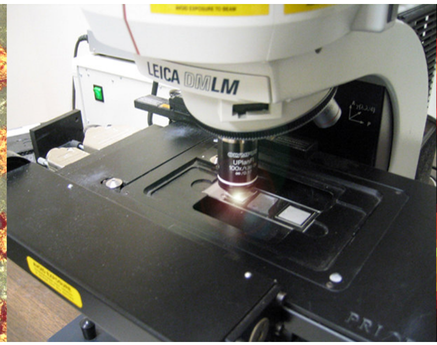
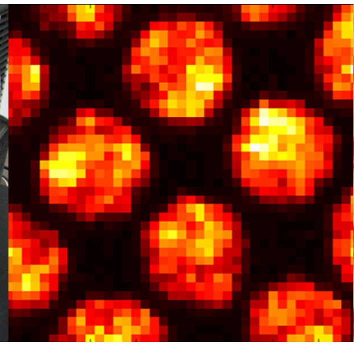
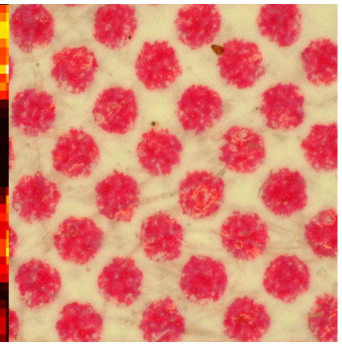








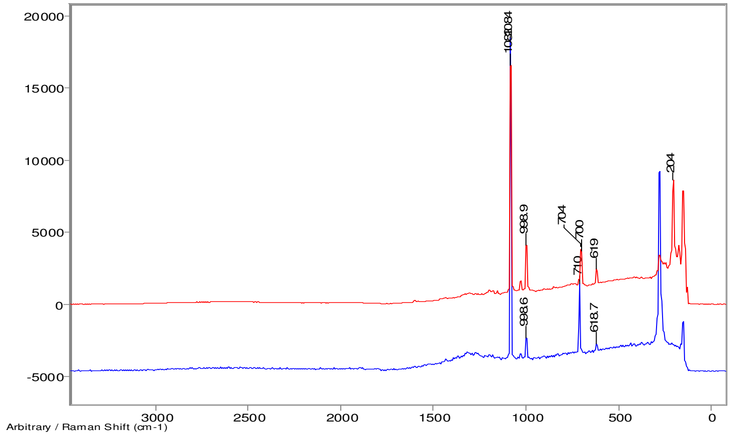
Confocal Raman microscope (785nm)

- light scattering technique
- sensitive to polarizable molecules
  - complements IR spectroscopy
- high spatial resolution (~1µm)
- moderate sensitivity (0.1-1 wt %)
- limited or no sample preparation

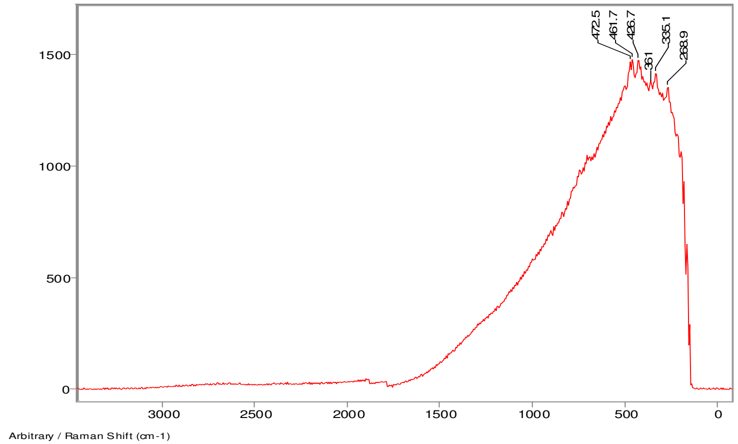
Raman in the analysis of coated papers

- identifiable coating components
  - $CaCO_3$(calcite / aragonite)
  - styrene based latices
  - TiO_2(anastase / rutile)
  - talc
  - kaolin in some cases (problems with fluorescence)
  - optical brighteners to some extent
  - etc.
- inks (pigments)
- coating colour (water is weak in Raman!)

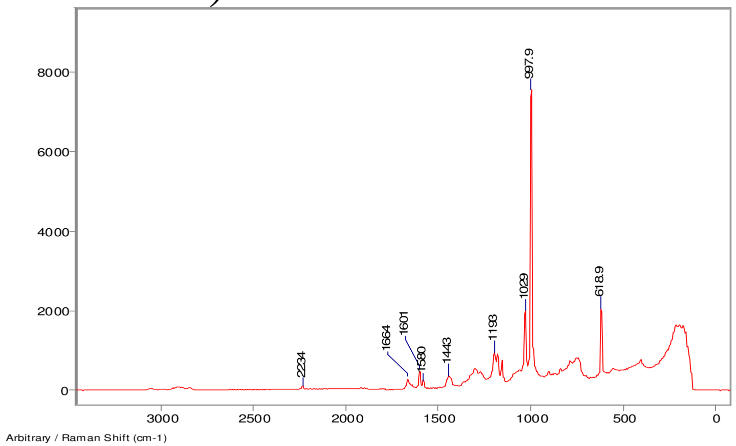
Raman spectra of coating colour components



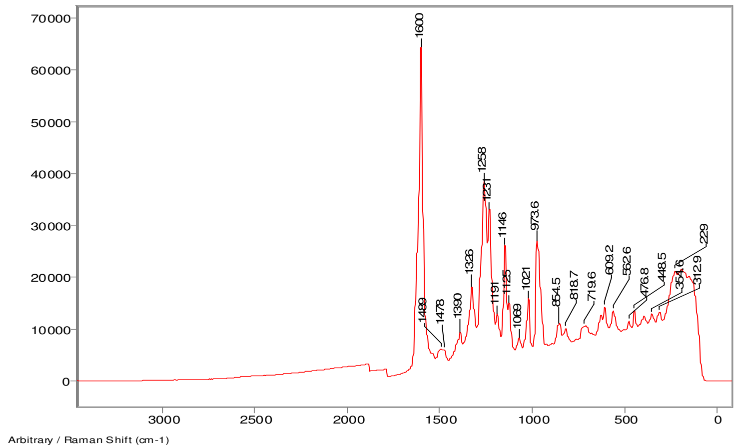
Coating: $CaCO_3$ (aragonite & calcite) & SB-latex



kaolin



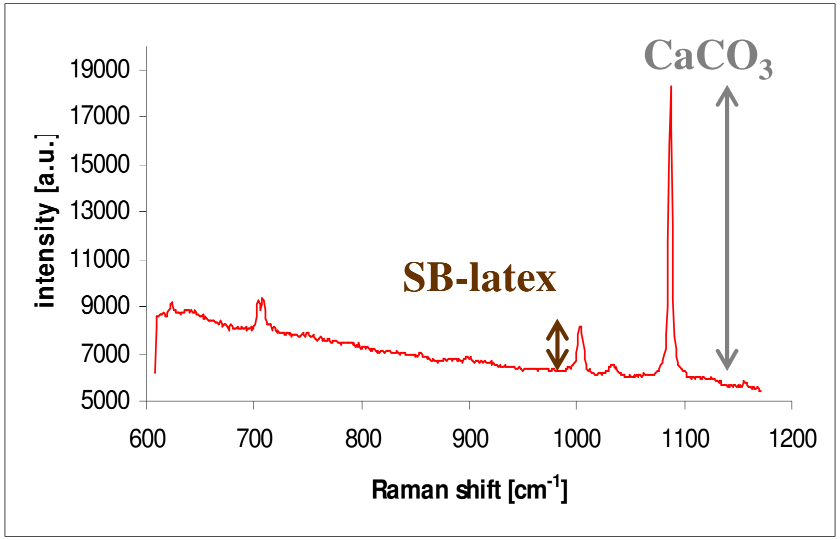
SB-latex



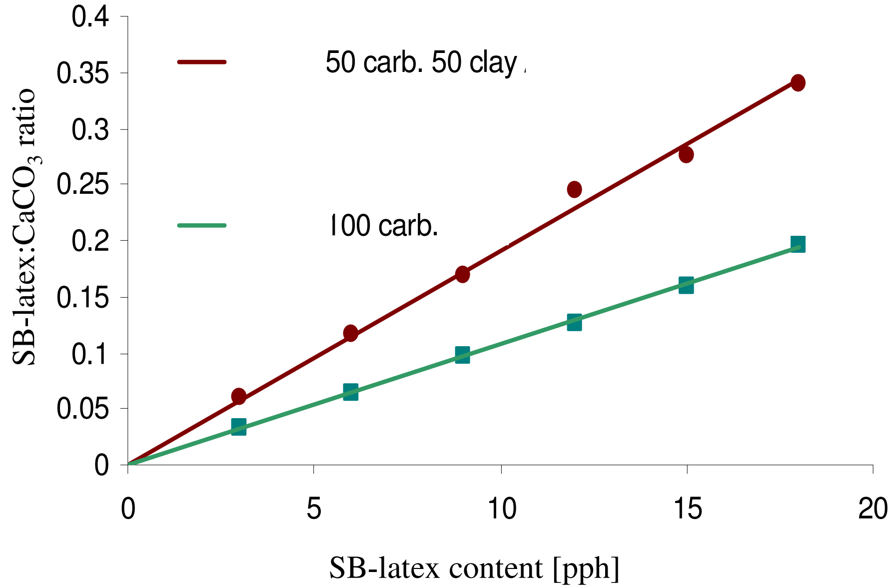
optical brightener

data analysis

peak height analysis

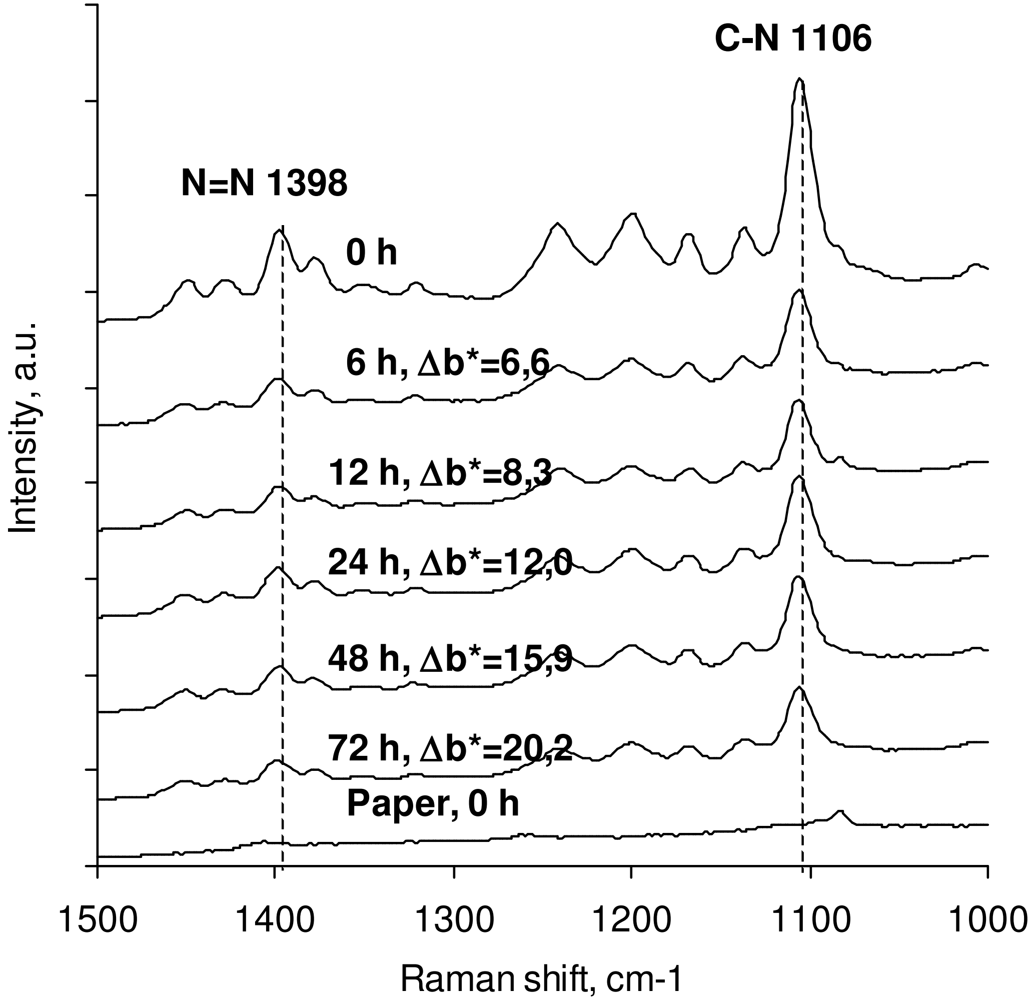


SB-latex:$CaCO_3$ peak ratios used in quantification



- calibration is straightforward
  - calibration for different pigment mixtures, pigments and latices
- no calibration if relative variation is sufficient
  - linear calibration lines

example – light fastness of ink-jet printed paper



- yellow light-exposed prints, kaolin-based coating
- the dye can be easily detected, i.e. N=N at 1398 cm^{-1}
- extended light exposure of the printed samples
  - intensity of the dye bands decrease
  - intensity changes correlate well with changes in print yellowness Δb*

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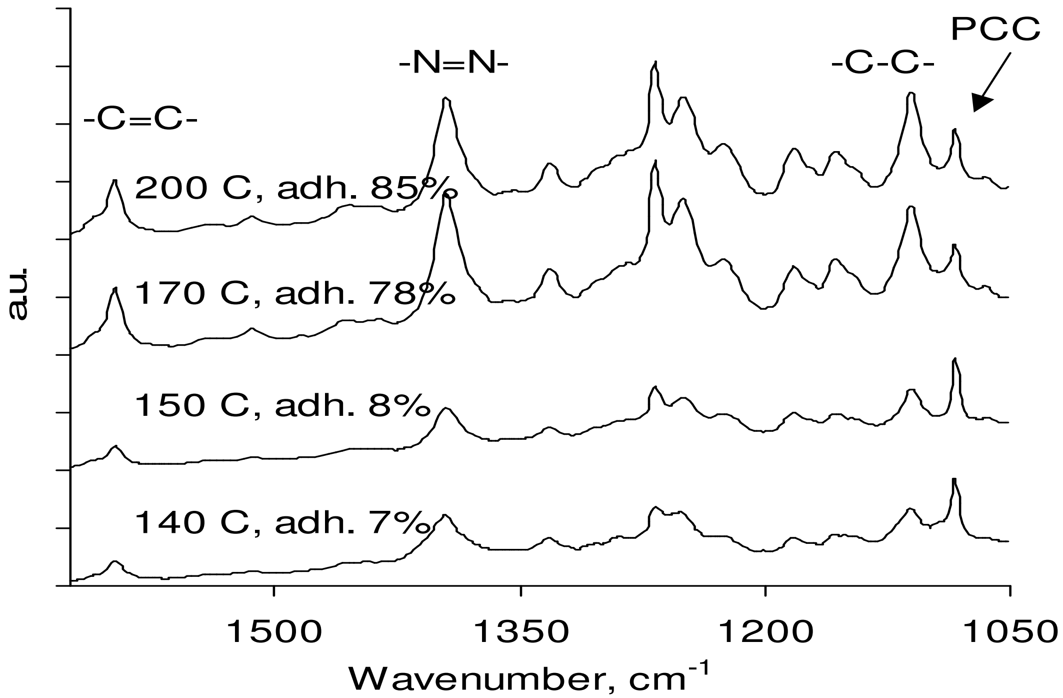
example - adhesion of electrophotographic print



- EG prints fixed at different temperatures (spectra at toner maximum)
- increase in the fixing temperature
  - pigment bands (N=N, C-C) strengthen in relation to the PCC band
  - intensity changes correlate well with the adhesion levels

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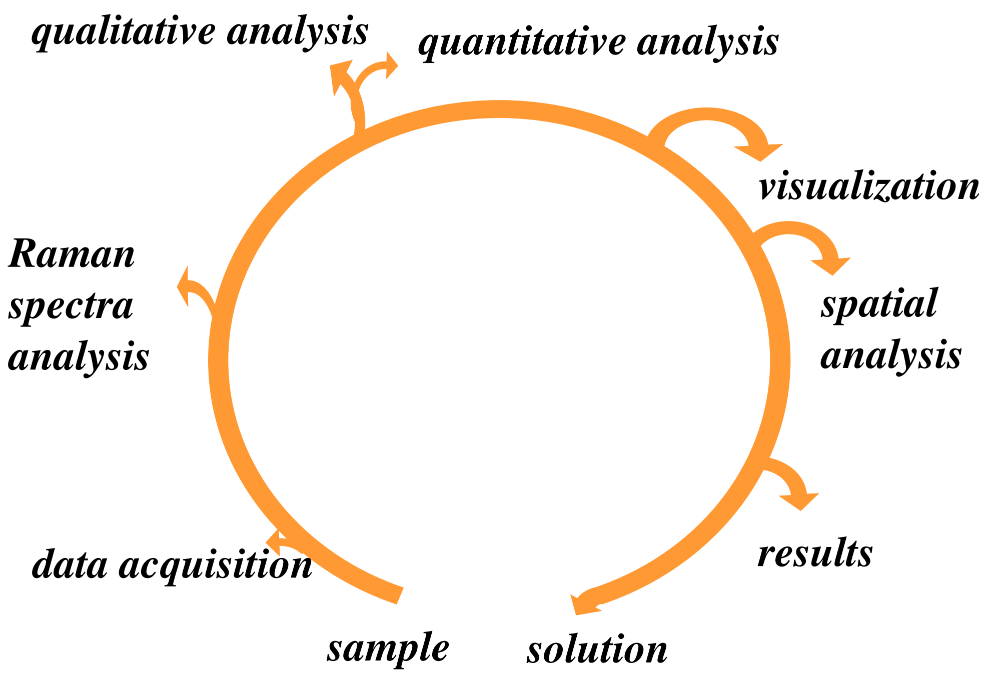
chemical mapping based on Raman



- operates usually in backscattering mode
- resolution can be varied
- surface vs bulk information
- inorganic and organic material analysis
- mapping of buried layers (e.g. under print)

Raman based mapping methods

- lateral mapping
  - imaging by point-by-point mapping
  - point-by-point mapping (points distributed over wider area)
  - imaging using filters
- depth profiling
  - direct depth profiling
    - traditional ”dry” method
    - immersion mehtod
  - line scanning of cross-sectioned samples

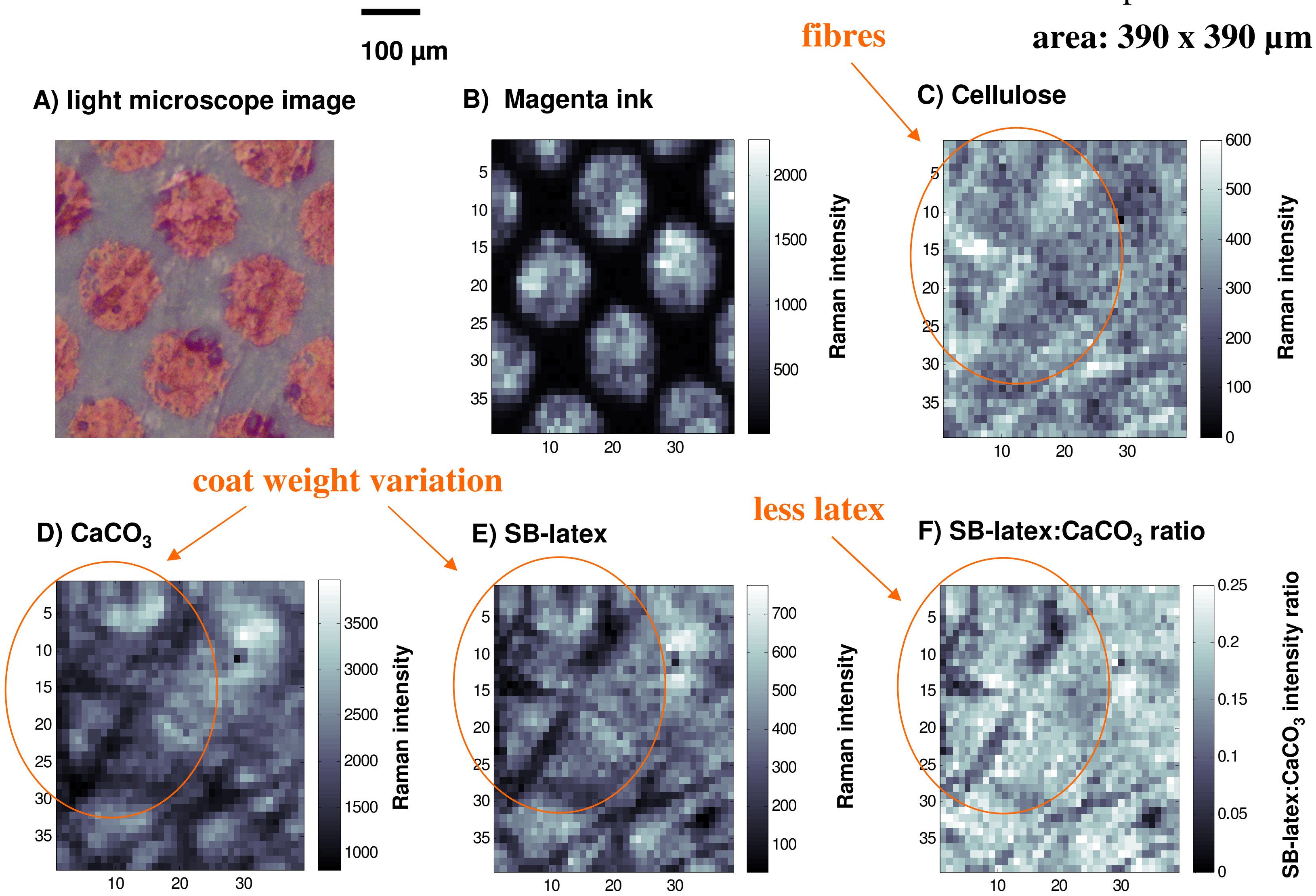
coating bulk imaging

pilot coated paper:

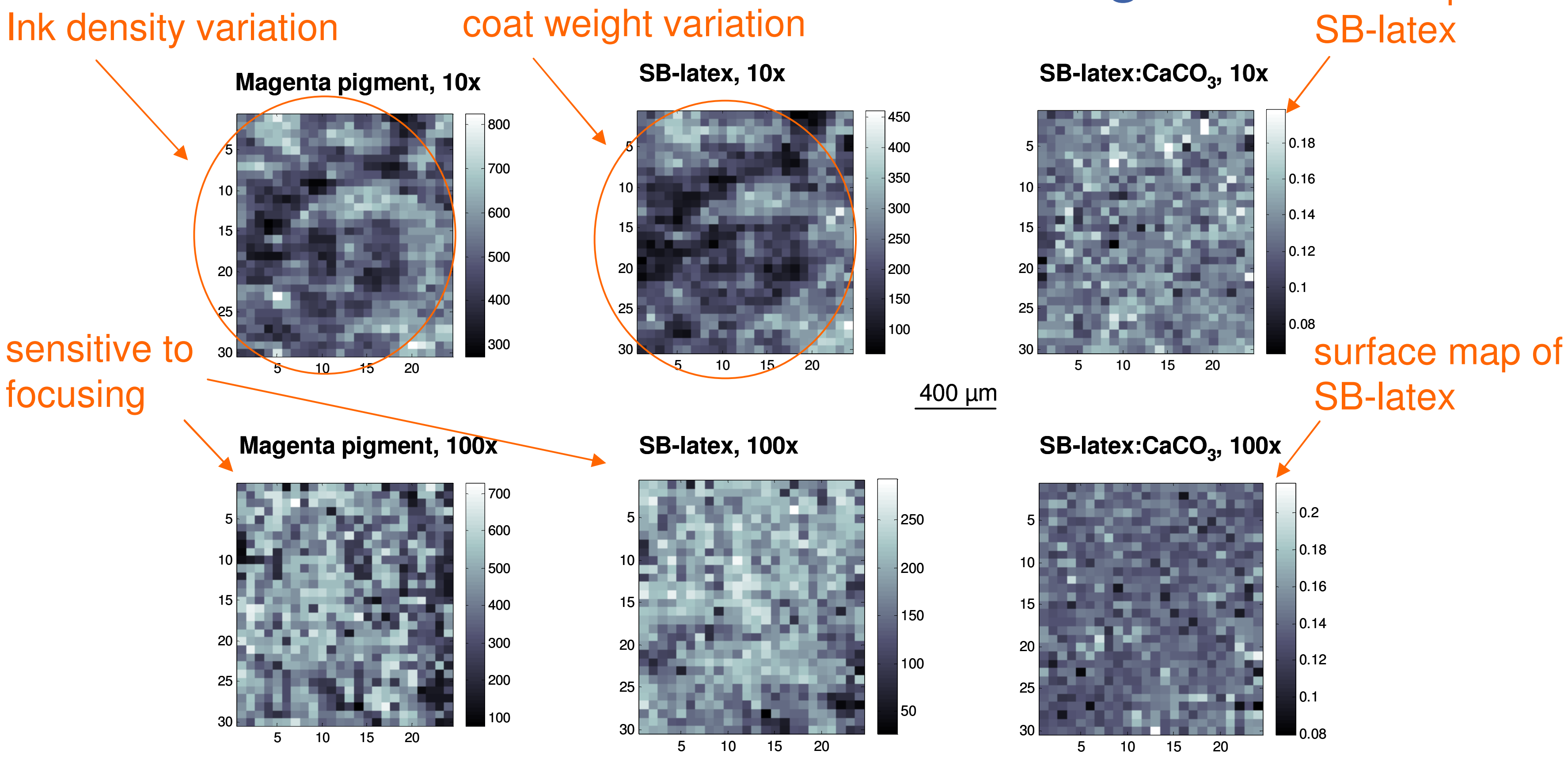
- 50 pph $CaCO_3$
- 50 pph kaolin
- 15 pph SB-latex

offset printed: 40% coverage

area: 390 x 390 µm



combination of bulk and surface images

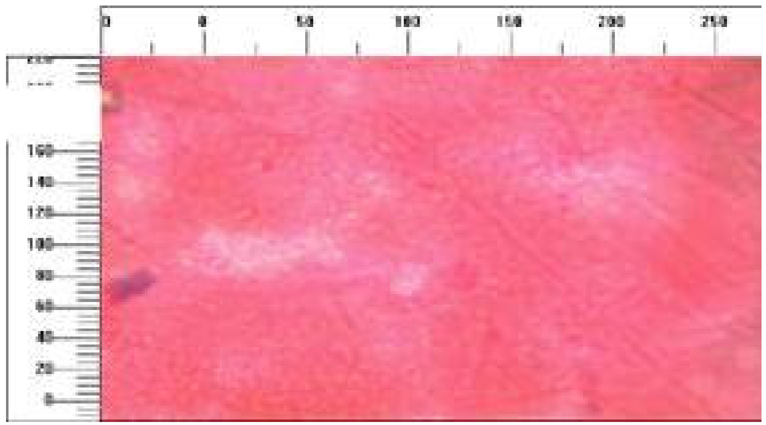


- same area but different objectives (coarse depth profiling)
- coat weight variation correlates with ink density variation, but no correlation with SB-latex
- average ratio values:10X objective 12.9 (±7.3%), 100X objective 12.8 (±7.9%).

back trap mottle – point-by-point mapping

bad sample (G)	high ink density area	low ink density area
SB-latex – $CaCO_3$ ratio x 40 [a.u.]	*15.8*	*15.8*
variation in big area [%]	*1.4*	*1.8*
variation in small area [%]	*6.5*	*8.8*

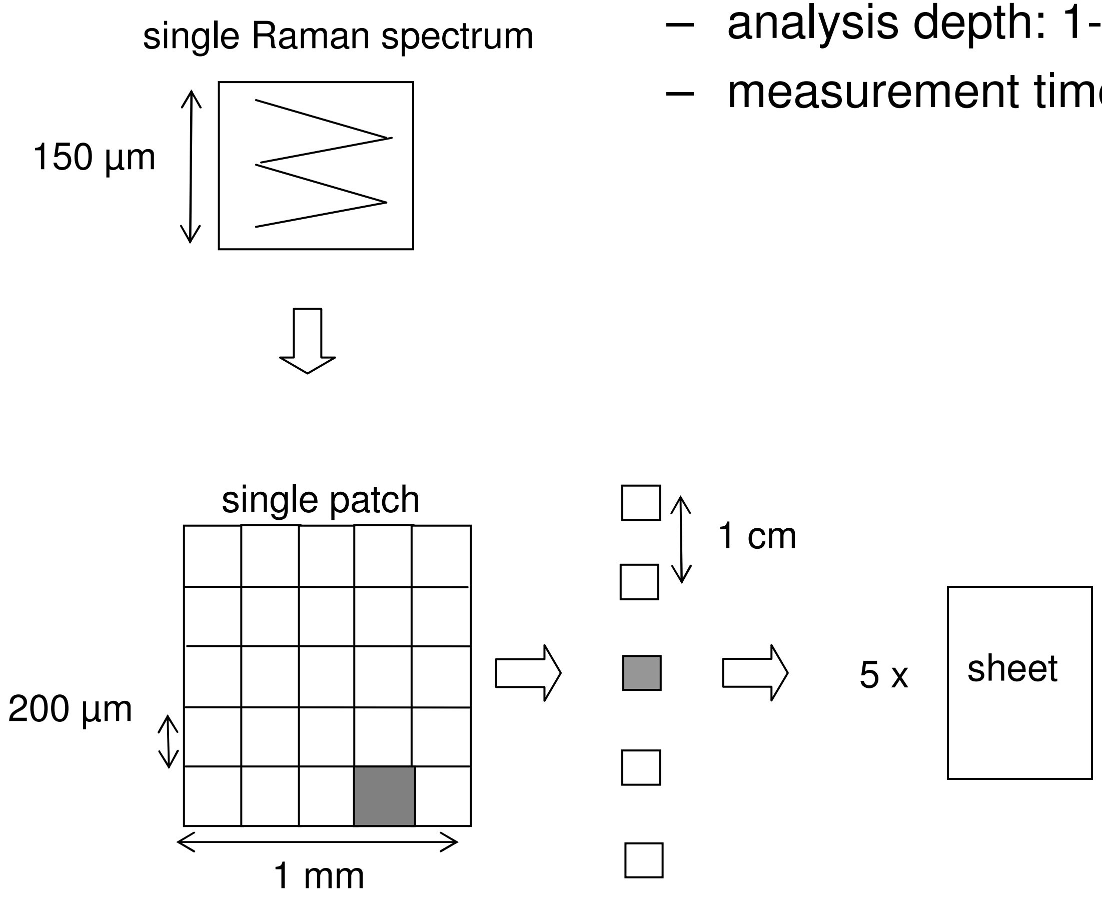
- 200 Raman spectra from high and low ink density areas (50X)
- no difference in SB-latex level in different ink density areas
- the difference in large area latex variation is small
- sample was also analyzed with LIPS, EDS, ESEM…[1]



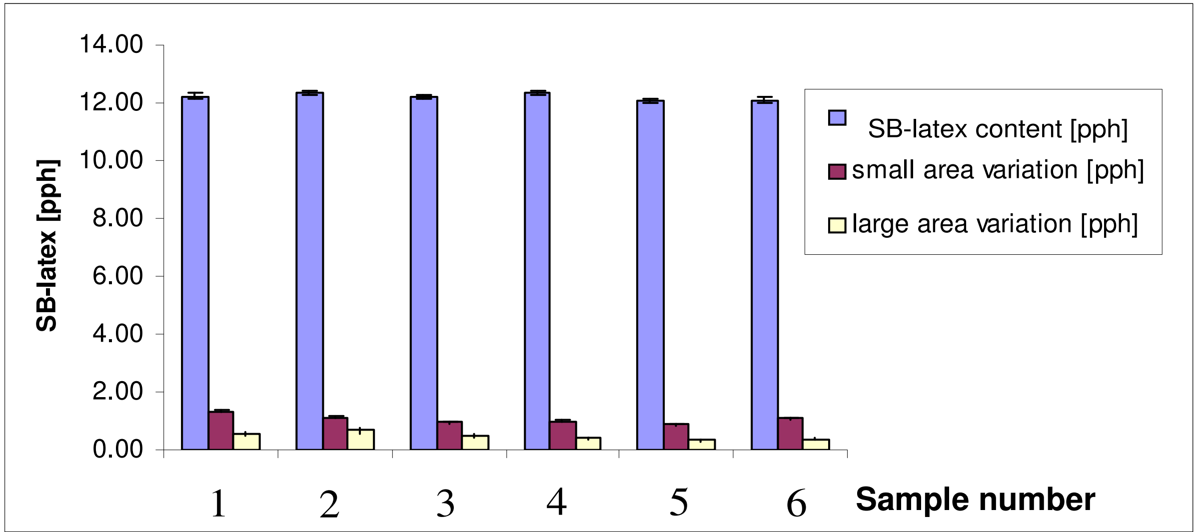
[1] Xiang, Y., et al. "The Cause of Backtrap Mottle: Physical or Chemical", Tappi 2000 Coating Conference.

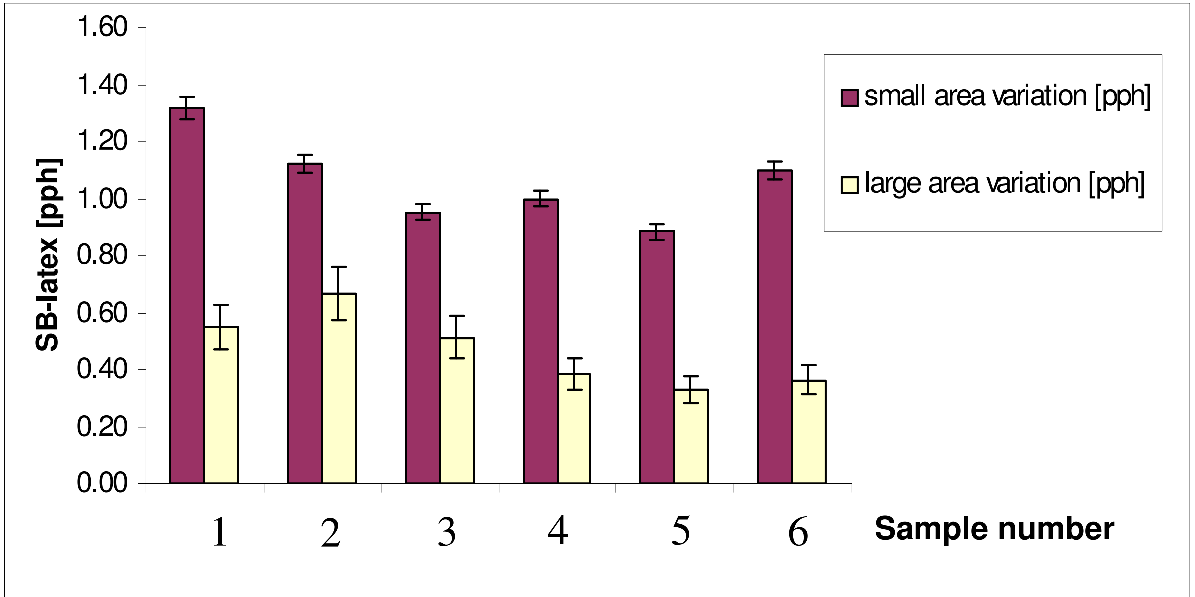
surface mapping - measurement scheme for SB-latex variation analysis(100x)

- analysis depth: 1-2 µm
- measurement time / sample: ~ 10 h



example - coating surface analysis results





- same coating formulation
- coating method and base paper properties were changed

⇒ mean SB-latex values similar

⇒ small differences in latex variation

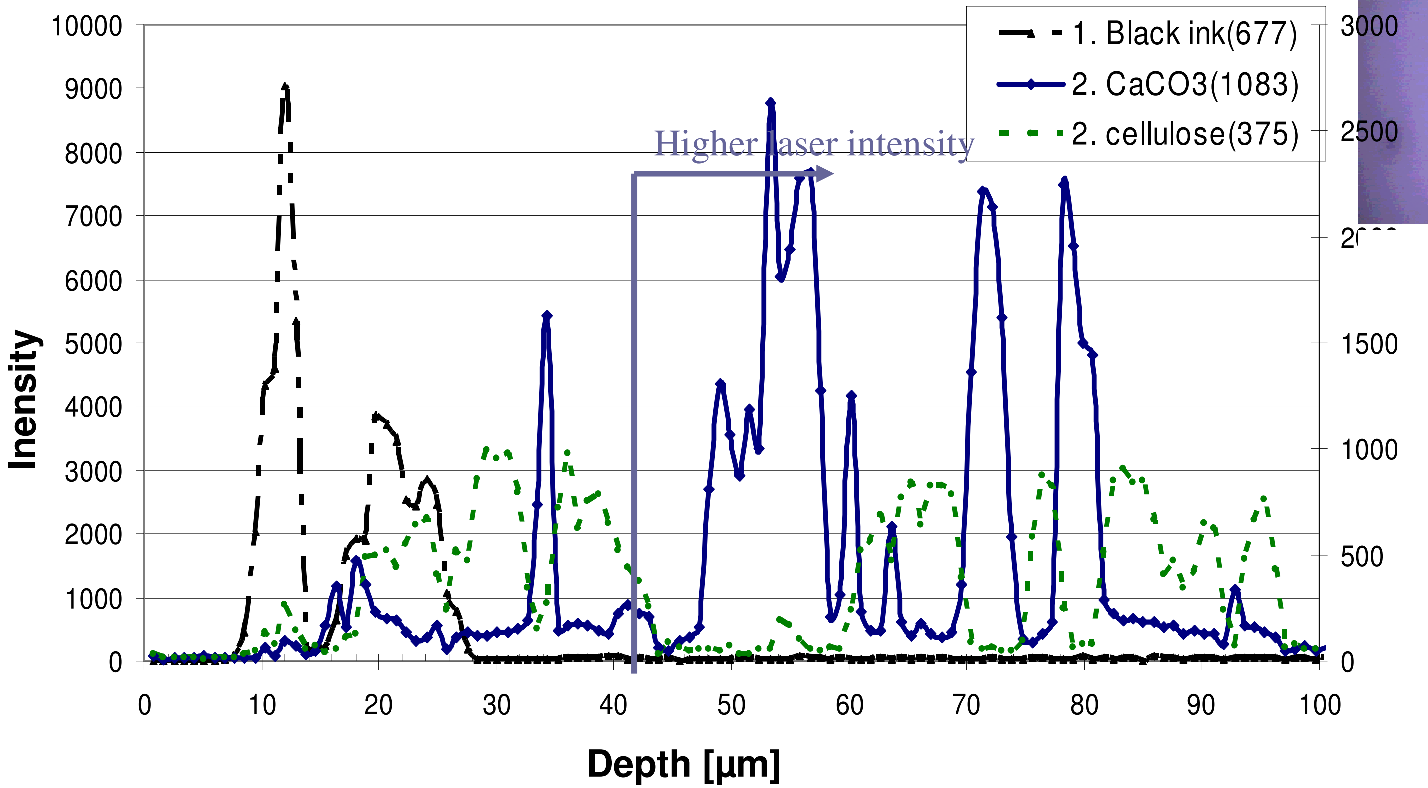
lateral mapping summary

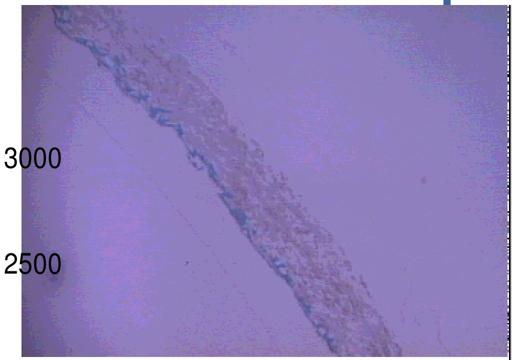
- chemical and structural information
- analysis depth is objective (and sample) dependent
- no sample preparation
- imaging is time consuming

Applications

- latex content and distribution
- coat weight and ink density variation & correlation to SB content

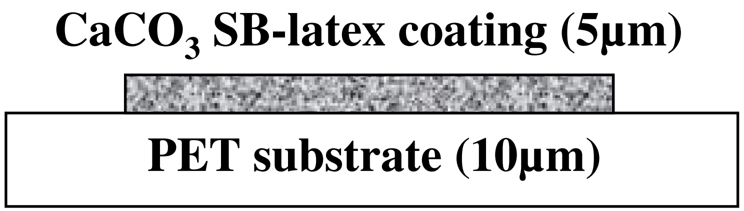
depth profile of cross-sectioned sample



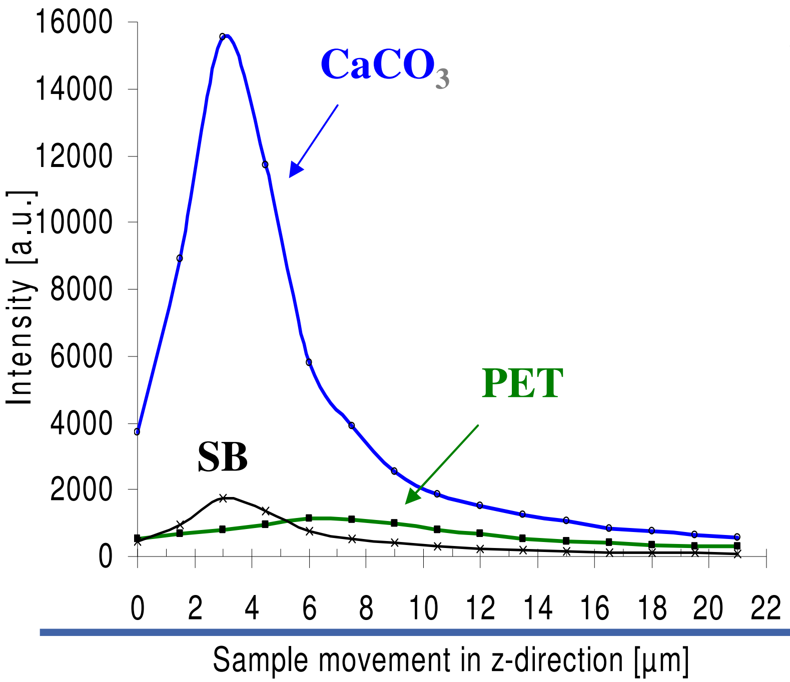


- flexoprinted envelope paper (uncoated, $CaCO_3$ filler)
- black ink burned easily (laser power was decreased)

depth profiling of paper coating - traditional method

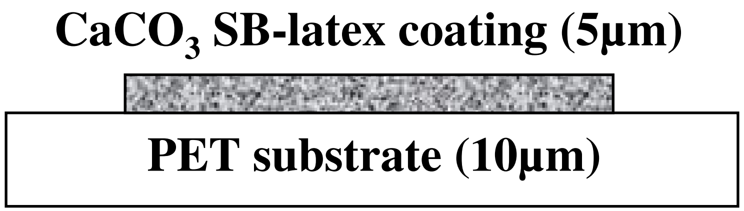


traditional method



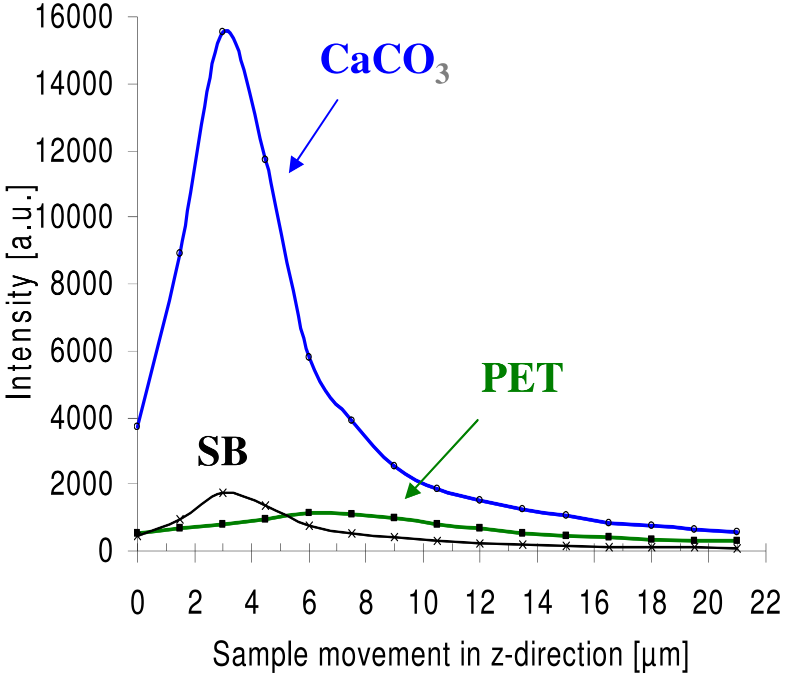
- low signal through light scattering coating

depth profiling of paper coating – immersion method

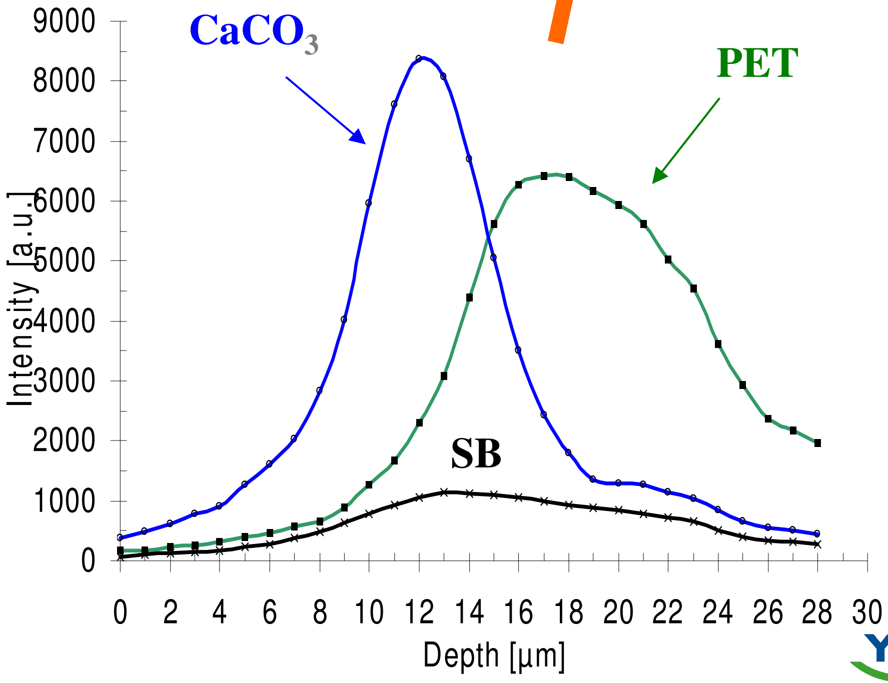


- signal through light scattering coating

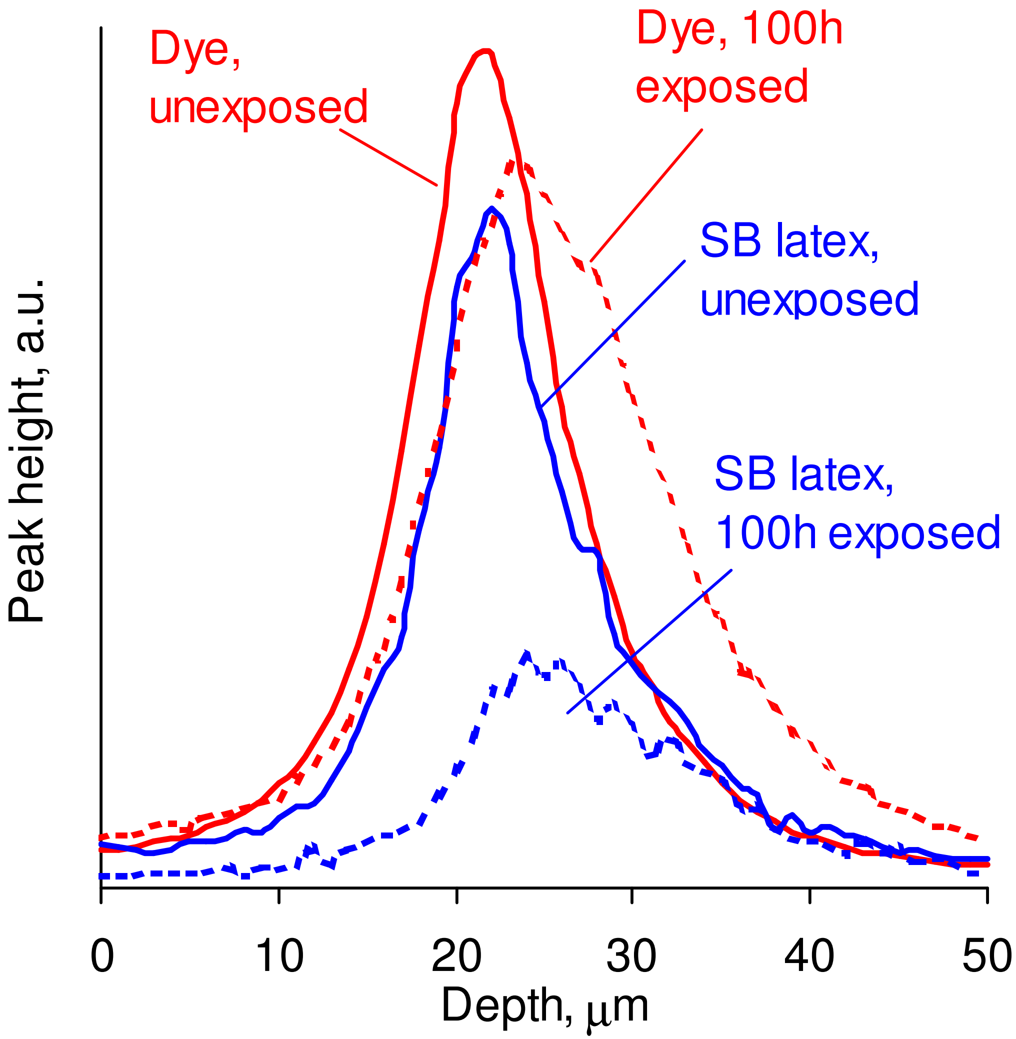
traditional method



immersion method



depth profiling through ink jet print



- magenta dye on kaolin-SB-latex coating
- light exposure 100h:
  - dye and SB latex decompose from the surface layers of the coating
  - dye and the aromatic moieties of latex seem to degrade as a result of light exposure

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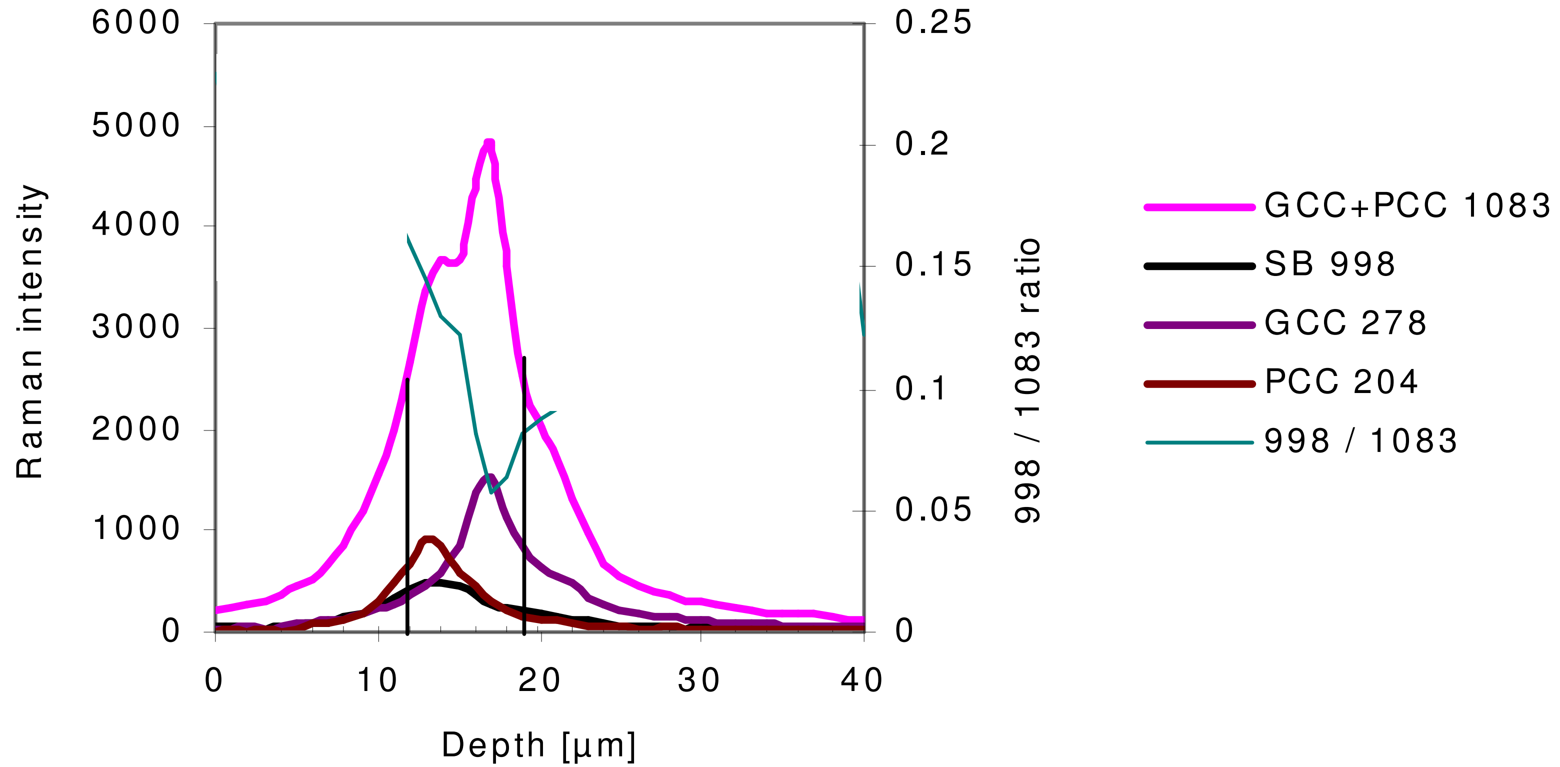
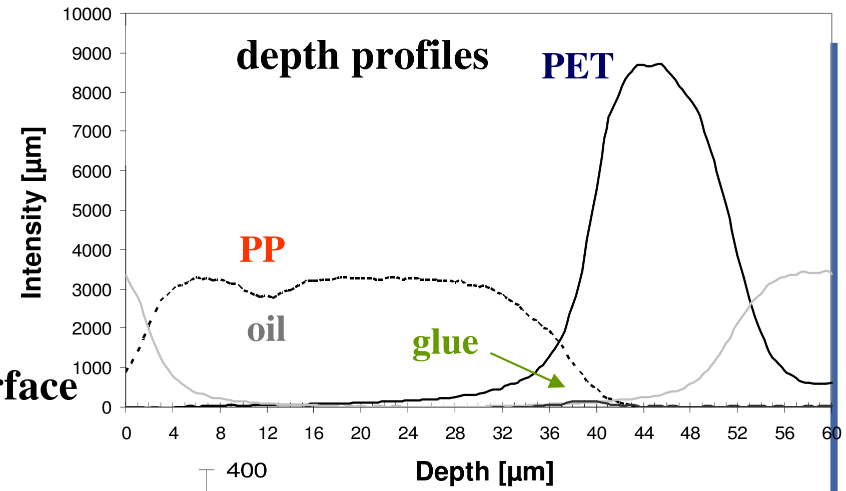
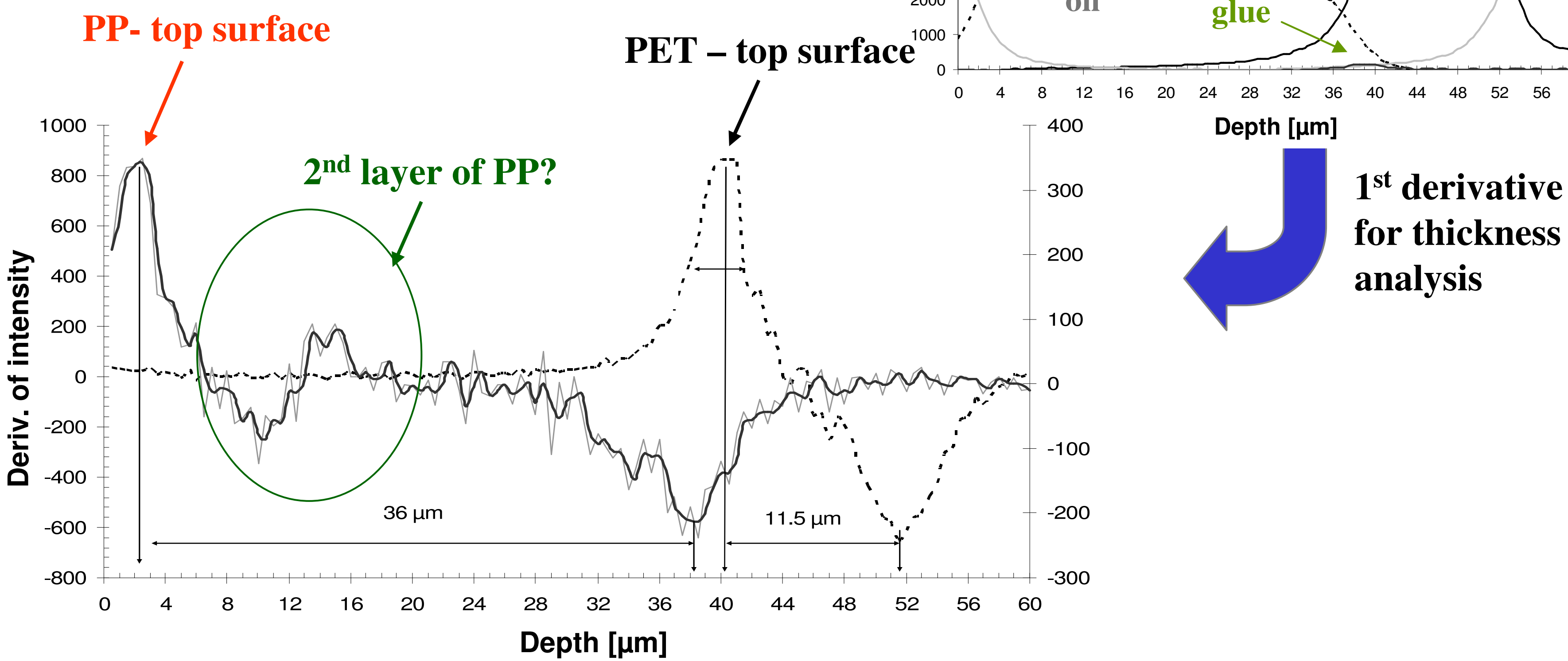
double coated paper



- precoat: GCC (calcite) & SB-latex
- top coat: PCC (aragonite) & SB-latex
- aragonite and calcite give separate Raman bands

thickness analysis





- PP-glue-PET layer thicknesses: 37 – 2.5 – 12 µm
  - PP-layer consisted of four layers 6-6-20-6 µm, each layer had different amount of additives (thicknesses given by polymer film manufacturer)

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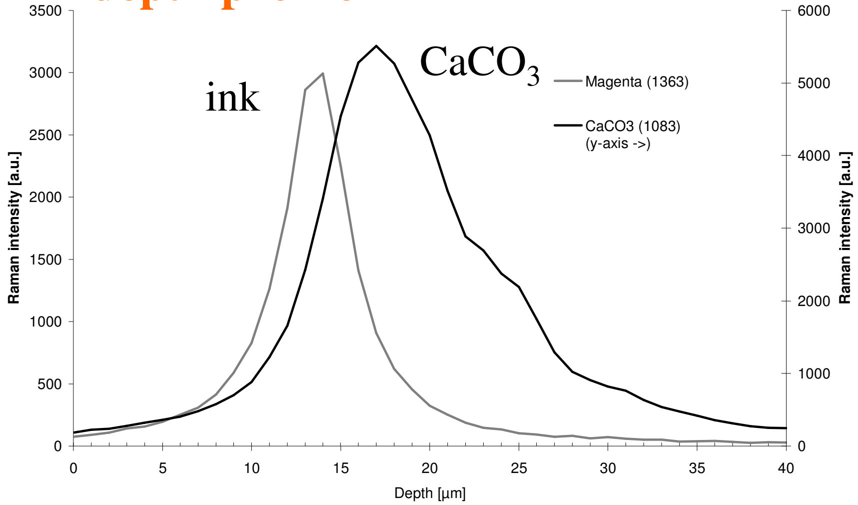
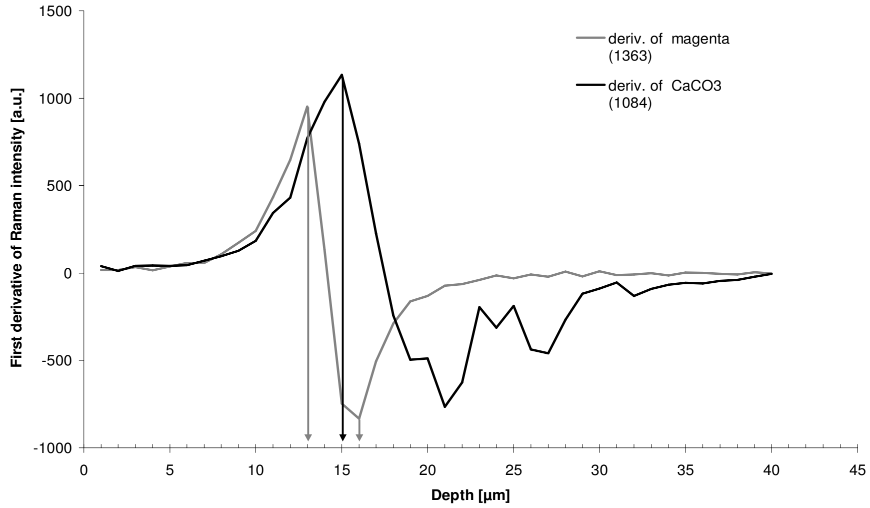
depth profiling through offset print

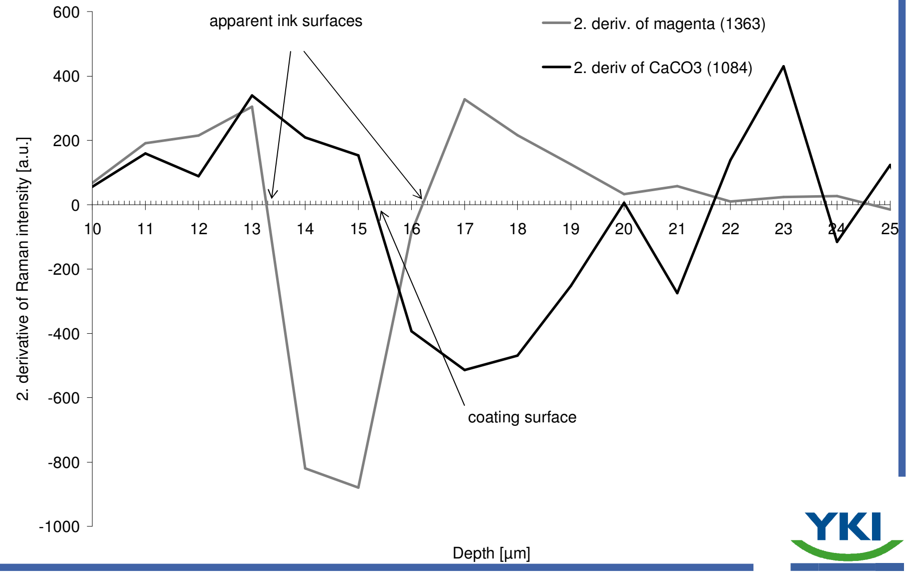
depth profile



1st derivative



2nd derivative



- through magenta and yellow
- apparent ink layer thickness
  - only if thickness > 2µm
- SB-latex content / distribution under ink

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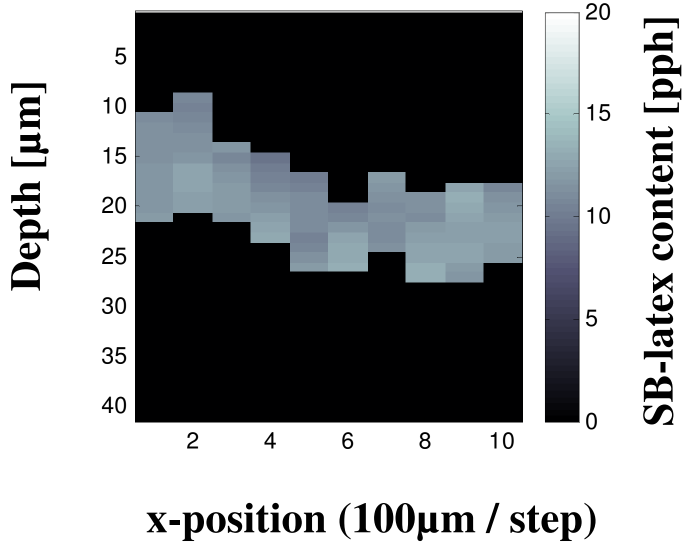
cross-section depth profiling

CLC coating:
- $CaCO_3$ 100 pph
- SB-latex 12 pph
+ additives

target coat weight: 2x9 g/m²



1 mm line in x-direction

measurement time: 2 h 15 min

Data analysis:

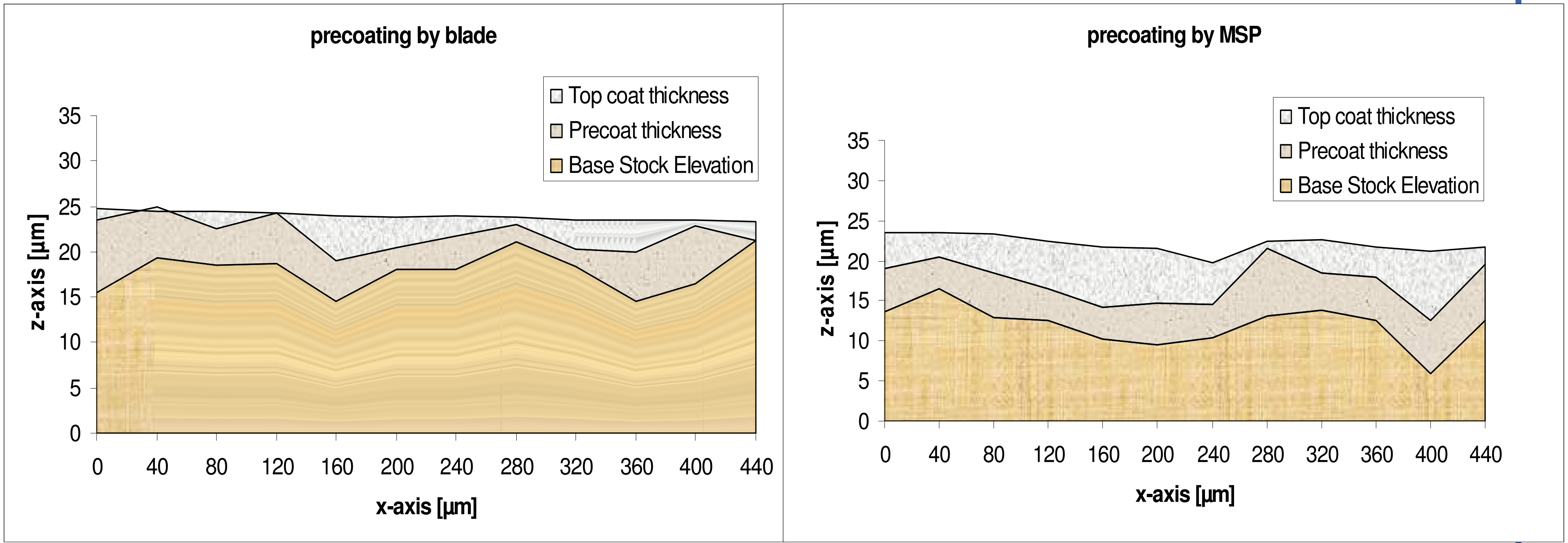
average thickness ≈ 9 µm

surface SB: 11.3 pph

bottom SB: 12.6 pph

average SB: 12.0 pph

MSP vs. blade in precoating – thickness profiles



- precoat by blade or MSP: GCC (calcite) & SB-latex
- top coat by blade: PCC (aragonite) & SB-latex
- depth profiles measured every 40 µm

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depth profiling summary

- 4 µm nominal z-resolution
- max. analysis depth 20-60µm
- simple sample preparation (no physical damage)

Applications:

- SB-latex distribution in z-direction
- layer thickness analysis (> 2 µm)
- analysis through ink (SB-latex content under defect etc)

conclusions

- Raman provides wide variety of techniques for paper coating analysis
- different chemical imaging and mapping techniques
- qualitative / quantitative analysis
- surface and bulk analysis
- analysis of buried layers (coating under print etc.)

⇒ Raman technique is now well established for SB-latex analysis

⇒ useful technique for coated and printed paper analysis

⇒ non-destructive → can be combined with other techniques

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references

- *Vyörykkä, J.*, **Confocal Raman microscopy in chemical and physical characterization of coated and printed papers**, *D.Sc. thesis, accepted for publication (2004)*
- *Vyörykkä, J., Juvonen, K., Bousfield, D., Vuorinen, T.*, **Raman microspectroscopy in lateral mapping of chemical and physical composition of paper coating**, Tappi Journal, 3(9), 2004, p.19
- *Vyörykkä, J., Bousfield, D., Vuorinen, T.,* **Confocal Raman microscopy: A non destructive method to analyze paper coating depth profiles**, Nordic Pulp and Paper Research Journal, 19(2), 2004, p.218.
- Sundqvist, H., **Structure and CSWO printing press runnability of a matt LWC paper grade – Raman spectroscopic approach**, M.Sc. Thesis, Helsinki University of Technology, Finland, 2003, 110 p
- *Bitla, S., Tripp, C.P., Bousfield, D.W,* **A Raman Spectroscopic Study of Migration in Paper Coatings,** Journal of Pulp and Paper Science, 29(11), 2003, p 382
- *Vikman, K., Sipi, K.,* **Applicability of FTIR and Raman spectroscopic methods to the study of paper-ink interactions in digital prints,** Journal of Imaging Science and Technology, 47(2), 2003, p 139
- *Vyörykkä, J., Paaso, J., Tenhunen, M., Tenhunen, J., Vuorinen, T., Stenius, P.*, **Analysis of depth profiling data obtained by confocal Raman microspectroscopy**, Applied Spectroscopy, 2003, Vol 57, No 9, p 1123-1128.
- *He, P., Bitla, S., Bousfield, D., Tripp, C.P.*, **Raman spectroscopic analysis of paper coatings**, Applied Spectroscopy, v 56, n 9, September, 2002, p 1115
- *Vyörykkä, J., Iitti, H., Vuorinen, T., Stenius, P.,* **Raman microspectroscopy in the lateral mapping of paper coating composition**, 2002 Coating and Graphic Arts conference and Trade Fair, Orlando, USA, May 6-8, 2002, TAPPI, p. 265-271.
- *Vyörykkä, J., Halttunen, M., Iitti, H., Tenhunen, J., Vuorinen, T., Stenius, P.,* **Characteristics of immersion sampling technique in confocal Raman depth profiling**, Applied Spectroscopy, 2002, Vol 56, No 6, p. 776-782.