

# Quantitative in-line measurements on papers

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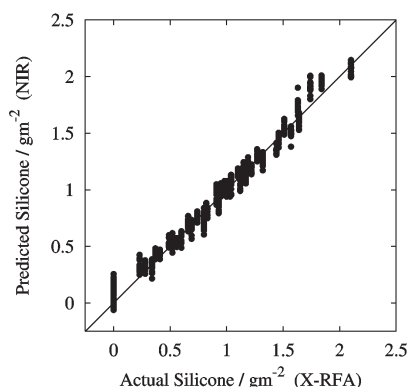
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## Introduction

In the paper industry, as well as in the analysis of paper related goods, near infrared (NIR) methods have been described for the control of incoming materials.<sup>1</sup> Quantitative models for the components in papers such as mechanical pulp (TMP, CTMP = chemically/thermally mechanical pulp, containing lignin) or chemical pulp (= classical types of cellulose) and the various detectable filler materials (clay, talc, chalk) or coatings thereof have been shown.<sup>1,2</sup> Much more sophisticated applications involve measurement of additives in papers, for example, sizing agents (resin size, AKD<sup>3</sup>) and wet or dry strength materials.<sup>3</sup> Moreover, the characterisation of paper by their physical properties, including absolute moisture,<sup>4</sup> ash content,<sup>4</sup> basic weight<sup>4</sup> and thickness,<sup>4</sup> as well as tear index,<sup>5,6</sup> tearing strength,<sup>5</sup> bursting strength,<sup>6</sup> tensile stretch,<sup>5</sup> tensile strength,<sup>6</sup> fibre length,<sup>5</sup> debonding energy,<sup>6</sup> hydrophobicity (Cobb by Ultrasound),<sup>6</sup> wettability<sup>6</sup> and printability<sup>6</sup> is possible. Apart from these applications, NIR spectroscopy could be a new tool to classify waste paper during the screening process. In this study, the feasibility to set up in-line NIR methods for products converted from papers is presented. Silicone coated papers are widely used as release liners, with the major application being stick-on labels of all types. Besides the quantification of coat weights from adhesives, it is especially important to control closely a fixed amount of around  $1 \text{ g m}^{-2}$  silicone applied, because too little will be ineffective and too much is a waste of expensive material.<sup>7,8</sup> To make direct implementations for product consistency and efficiency of the process, in-line monitoring of coat weights by realistic calibration models is required. All the variations from paper, due to the substrate, colour or opacity and basic weight, have to be considered in order for the measurement procedure to be robust enough for paper change at the web. The creation of a comprehensive, but selective, calibration model for silicone (Figure 1) has already been successfully made with an at-line FT-NIR spectrometer based on the VECTOR 22/N, Bruker Optik GmbH (data set C, Table 1). To meet the requirements in-line during label stock production in



**Figure 1. Comprehensive calibration model for silicone (set C).**

**Table 1. Validation results of quantitative models for the determination of silicone coat weights on glassine papers.**

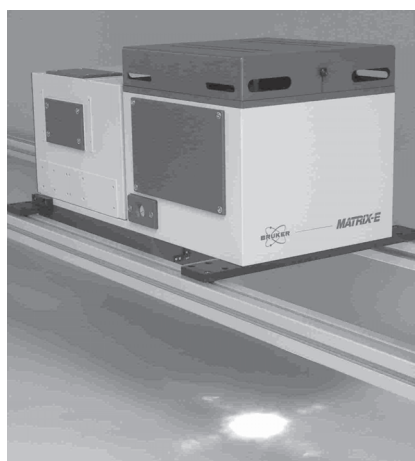
| Quantitative Model        | Kind of Validation | Silicone Coat weight range gm <sup>-2</sup> | Number of spectra | Data pre-processing                          | Frequency cm <sup>-1</sup> | Number of PLS terms | Coefficient of Determination <i>R</i> <sup>2</sup> | <i>RMS</i> Error Validation g m <sup>-2</sup> |
|---------------------------|--------------------|---------------------------------------------|-------------------|----------------------------------------------|----------------------------|---------------------|----------------------------------------------------|-----------------------------------------------|
| At-line Set A Figure 1    | Test-Set           | 0–2                                         | 1,320 individual  | 1 <sup>st</sup> derivative 5 point smoothing | 7501–4015                  | 7                   | 97.9 %                                             | 0.07                                          |
| In-line Set B Figure 5(a) | Cross              | 0.75–1.43                                   | 12 average        | Vector normalisation                         | 6101–5446                  | 6                   | 99.8 %                                             | 0.01                                          |
| In-line Set C Figure 5(b) |                    | 0.77–1.45                                   | 13 average        | +                                            |                            | 2                   | 97.2 %                                             | 0.03                                          |
| In-line Set C Figure 6(a) |                    |                                             | 326 individual    | 1st derivative (17 point smoothing)          |                            | 4                   | 96.9 %                                             | 0.04                                          |
| In-line Set C Figure 6(b) |                    |                                             | 350 individual    |                                              |                            | 9                   | 95.5 %                                             | 0.06                                          |

the coating machine, a new concept for an FT-NIR spectrometer was designed to perform the measurements of moving paper in a non-contact mode.

## Materials and methods

### Instrument

The new FT-NIR spectrometer, MATRIX-E, was developed by Bruker Optik GmbH, Ettlingen, Germany. The MATRIX-E is equipped with four lamps to illuminate the moving paper web in the machine. The angle of incidence was chosen so that the contribution due to specular reflection is minimized. The extended illuminated area of 25 diameter (Figure 2) is suitable, in general, to scan large and inhomogeneous samples during movement. Due to the small thickness of the backing papers (= glassine papers) for labels, the light penetrates the sample twice as it is reflected by the roll made from metals such as aluminum or chrome. This reflection introduces a matrix-effect in the NIR spectra and it is important that the kind of metal used is specified. After interac-



**Figure 2. FT-NIR spectrometer MATRIX-E illuminating the sampling area.**

tion with the sample, the diffusely-scattered light returns to the instrument and is directed to the detector (InGaAs Peltier cooled, operating range 12,800 to 4,000  $\text{cm}^{-1}$  or 780 to 2,500 nm). The optimum spatial distance from the measurement window to the sample is 170 mm but slight differences are not relevant to acquire reproducible spectra. Spectralon, built inside the instrument, is used as an internal reference material. The internal background acquisition is performed by closing the instrument with a shutter automatically and making installations in the production environment more stable.

### NIR Experiment

The scan time for in-line measurements of the MATRIX-E was set to five seconds per NIR spectrum (32 scans, spectral resolution 16  $\text{cm}^{-1}$ , scanner velocity 20 kHz). For internal reference acquisition, the shutter closes at variable time intervals (for example, every 30 minutes) and records a background spectrum. The velocity of the paper machine was 400  $\text{m min}^{-1}$ , which corresponds to a length of 33.3 m paper per spectrum. If the machine velocity is different, or becomes faster in the future, the paper will run more quickly through the dryers and changes will result in its temperature or moisture content introducing additional matrix-effects in the NIR spectra. However to develop robust models, “artificial spectral variations” can be created by changing the moisture content in a paper sample but using the same reference value for silicone coat weight (as reported in a previous NIR study albeit from the agricultural sector).<sup>9</sup>

For this in-line experiment, 13 coat weights from silicone ranging between 0.73 to 1.45  $\text{g m}^{-2}$  were set at the coating machine supplying one type of glassine paper. The glassine paper was measured before the initial coating with silicone in the machine as well. Influences from vibrations caused by the movement of the paper are kept to a minimum as the scanning is performed on a roll. Moreover, measurements recorded with the MATRIX-E are insensitive to vibrations by the machinery itself. The same observation was made with interference from high voltage equipment. A movement of the MATRIX-E across the web is considered in the future to ensure a flat, uniform coating.

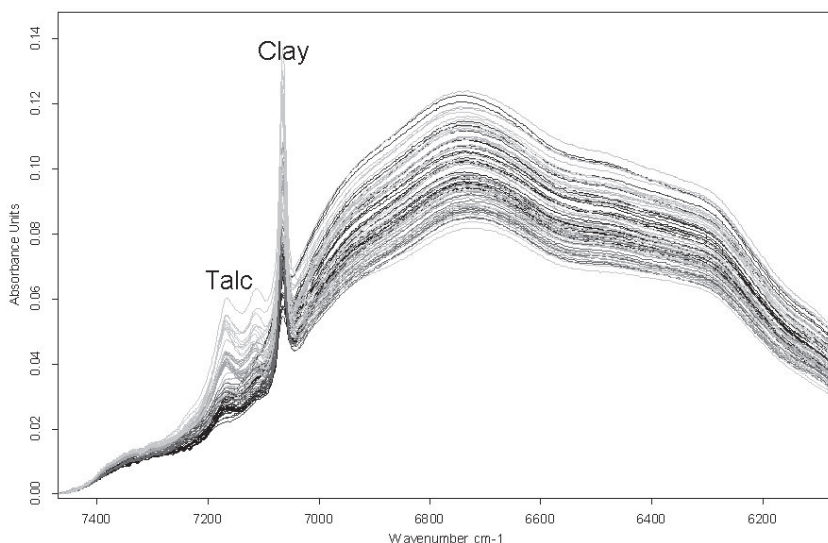


Figure 3. NIR spectra from silicate coated papers showing significant OH absorption bands.

### Reference analysis

Sampling methods for the element silicon (Si) by X-ray technology are available and require calibrations as well. This XRF analysis is rather time-consuming (two minutes in total) and depends on the surrounding temperature. Moreover, it cannot distinguish between silicate present in clay- or talc- coated papers (Figure 3) and organic silicone compounds provided for the coating. Clay-coated papers are often used as a backing paper for labels and their silicone coat weight is either not examined at all or could be calculated indirectly from the central element {aluminum in clay  $Al_2[Si_2O_5](OH)_4$ }. In addition, the delay between actual production and off-line XRF-analysis prevents immediate actions onto the process.

After in-line measurements with the MATRIX-E, lab sheets from the end product of self-adhesive

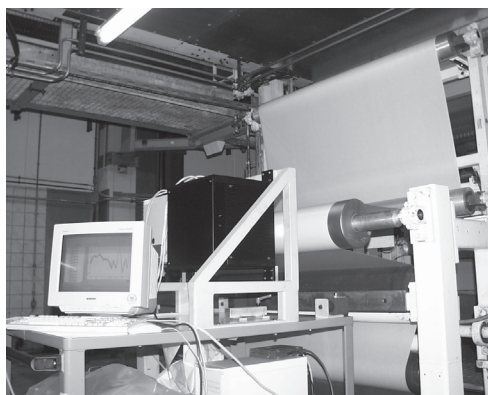


Figure 4. MATRIX-E installed in label stock conversion facility at the paper roll.

**Table 2. Reference values of silicone from two different XRF analyses: 1st set A (single analysis, same day), 2nd set B (averages from six replicates, a few days later).**

| Machine Setting                             | 1 <sup>st</sup> XRF analysis | 2 <sup>nd</sup> XRF analysis |
|---------------------------------------------|------------------------------|------------------------------|
| Silicone Coat weight range gm <sup>-2</sup> | 0.75 – 1.43                  | 0.77 – 1.45                  |
| 0                                           | 0                            | 0                            |
| 1                                           | 0.75                         | 0.77 ± 0.03                  |
| 2                                           | 0.76                         | 0.78 ± 0.01                  |
| 3                                           | 0.79                         | 0.80 ± 0.01                  |
| 4                                           | 0.84                         | 0.88 ± 0.02                  |
| 5                                           | 0.88                         | 0.92 ± 0.01                  |
| 6                                           | 0.89                         | 0.94 ± 0.02                  |
| 7                                           | 0.97                         | 1.02 ± 0.01                  |
| 8                                           | 0.98                         | 1.02 ± 0.02                  |
| 9                                           | 1.00                         | 1.06 ± 0.01                  |
| 10                                          | 1.07                         | 1.12 ± 0.00                  |
| 11                                          | 1.16                         | 1.18 ± 0.01                  |
| 12                                          | 1.27                         | 1.30 ± 0.01                  |
| 13                                          | 1.43                         | 1.45 ± 0.02                  |

laminate were collected from each reel produced with a certain setting of silicone. These sheets were taken according to the MATRIX-E measurement position along the web (Figure 4). On the same day, a benchtop XRF analyser (Lab X 3500, Oxford Instruments Analytical, High Wycombe, UK) was used for a single analysis of the silicone value (data set A, Table 2). The same lab sheets were examined again carefully by the same Lab X 3500 a few days later (data set B, Table 2). From each sheet, six replicates alternating with an appropriate standard sample were measured. These six replicates were offset-corrected according to the standard sample and then the averages were calculated. In Table 2 the reference values for the same samples from both XRF analyses are given. Obviously the reference values depend on the time of the XRF measurements as their differences are larger than the absolute deviation between the replicates.

### Results and discussion

We compared the cross-validation results from two PLS-1-models (optimised with OPUS NT/QUANT Software by Bruker Optik GmbH) using the same average spectra for 13 settings but the two available reference values (Table 2) either from the first XRF-analysis on the same day and from the second XRF analysis a few

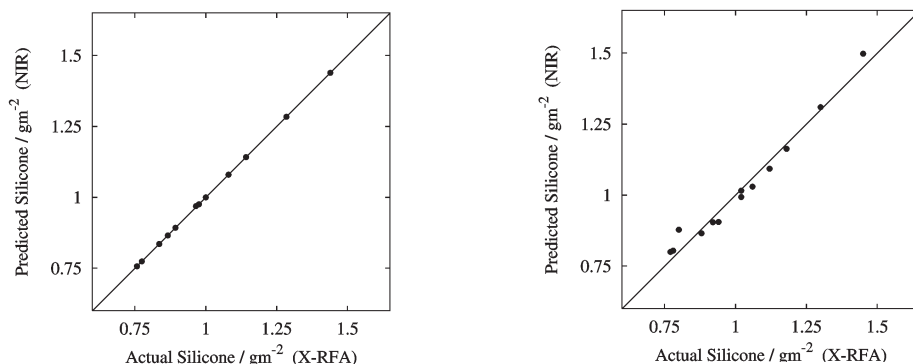


Figure 5. Comparison of PLS models from average spectra using different reference values.

days later (Figure 5). From the first model based on the single reference values, one outlier (Nr.3) was excluded. Nevertheless, this first model proves the feasibility and shows a better correlation  $R^2$  and predictive error  $RMSECV$  (Table 1) from cross-validation. Because the first XRF measurements were performed for each sample in a quick succession, they are not significantly affected by temperature changes. The second XRF analysis later is more susceptible to the temperature effect and leads to reduced accuracy in the PLS model.

In another comparison, two PLS-1 models from the individual spectra from in-line measurements were built, either with or without consideration of a zero point, from non-coated glassine paper. If the zero point is excluded, the quality of the model will improve, especially in terms of PLS-Vectors used (Figure 6, Table 1). The indication of the non-coated glassine paper spectra as outliers by the software can be explained by two reasons: firstly glassine paper has different scattering properties and no reflective silicone coating, which is even enhancing the signal (Figure 7) and, secondly, the zero point is too remote from the first coat weight setting of  $0.75 \text{ g m}^{-2}$  to be predicted reliably by the remaining set. As a consequence, the non-coated sample cannot be used for offset adjustments of a paper-type model after reel-to-reel-change.<sup>7,8</sup> However the paper type in one silicone coating machine will be changed up to 20 times per day and is currently supplied manually in a mode called “flying-web-change”. This

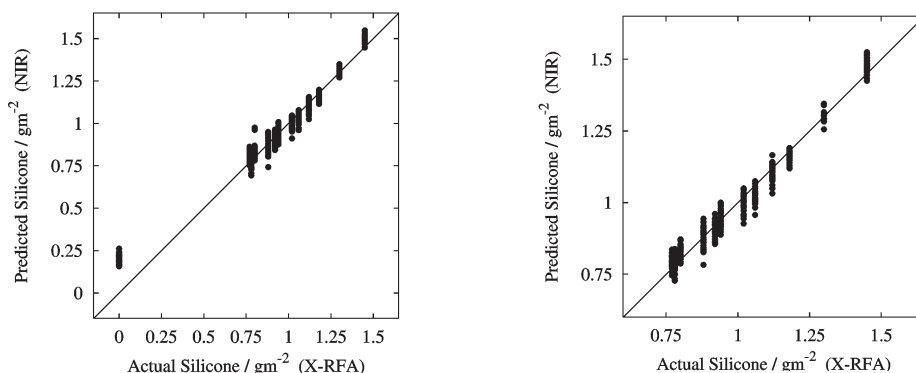


Figure 6. Comparison of PLS-models from individual spectra (a) with and (b) without zero.

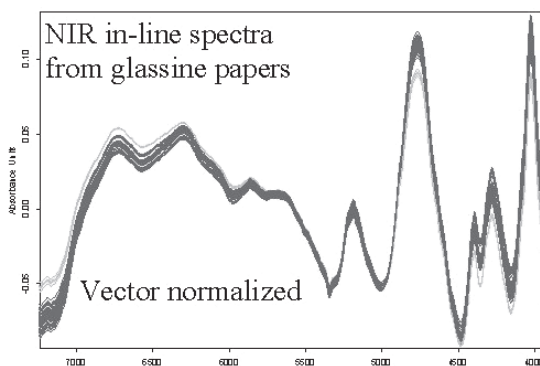


Figure 7. Differences in NIR-spectra from papers with and without reflecting silicone (light coloured spectra).

explains, once again, the demand for comprehensive calibration models without the need for offset adjustments.

## Conclusions

The present study shows the possibility of in-line calibrations for one paper type from low coat weights of silicone around  $1 \text{ g m}^{-2}$  during label stock conversion with a new FT-NIR spectrometer, MATRIX-E, in a non-contact mode. After an immediate reference analysis of lab sheets by X-ray technology required for PLS-evaluation, the statistical performances of the predictive model from averaged in-line spectra are  $R^2 = 99.8\%$  and  $RMSECV = 0.01 \text{ g m}^{-2}$  for silicone. The inclusion of a zero point from the non-coated glassine paper is not recommended. NIR spectra from other glassine paper types, including all the variations described above, are acquired in-line. The data are used to build one comprehensive in-line calibration model to meet the requirements for frequent paper change at the web, allowing continuous monitoring of an absolute value for coat weights from silicone. A realistic calibration model can be transported<sup>10</sup> to other MATRIX-E instruments to be installed in similar label stock production facilities without the need for instrument standardisation between the FT-NIR spectrometers.

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