

*Paolo Zanola, Ivano Alessandri,
Laura E. Depero
INSTM and Laboratorio di Chimica
per le Tecnologie
Università di Brescia
depero@ing.unibs.it*



NIR SPECTROSCOPY

For On-line Quantitative Analysis in the Textile Industry

NIR spectroscopy has been recently considered for the on-line quality control of different industrial sectors such as food quality assurance, polymer product quality, protein content of yeast cells, and quantitative moisture measurements.

In this paper we discuss the application of NIR spectroscopy in the textile industry for on-line quality control. In particular we present the application of chemiometric methods for quantitative analysis of the sizing agents content on synthetic fibers and we discuss the role of the water content in this kind of measurements.

Over the last 30 years Near InfraRed spectroscopy (NIR) has been increasingly used as an analytical tool [1] and is already used for on-line applications in different industrial quality controls such as food quality assurance [2-3], pharmaceutical industry quality control [4], protein and fat content in the meat [5] and quantitative moisture measurements [6]. This increasing popularity is due to the principal advantages of the method, namely speed, simplicity, and reliability of measurements. Indeed, this kind of measurement does not destroy the sample and does not require any particular preparation procedure. The main disadvantages of NIR have always been the minor intensity of absorption and the broadening of the absorption bands [6]. The latter drawback is

compensated by the rapid development of advanced and user-friendly software for multivariate analysis that allows to extract essential information for some properties of interest of the analyzed system from a large data set.

The use of multivariate analysis upon chemical measurements is often termed chemiometric and can be defined as "How to get chemically relevant information out of measured chemical data and how to present and display this information" (following the famous sentence of Wold).

In this work we discuss the use of NIR spectroscopy for on-line quality control in the textile sizing industry. This technique, combined with the chemiometric analysis, allows us to obtain quantitative measures of the percentage of sizing agents on the

synthetic textile fibers. Indeed, up to now, the quality control is typically done by sampling and using laboratory techniques, like chemical titration, that are destructive and take a lot of time. For this reason NIR spectroscopy opens huge perspective for the on-line quality controls thanks to his peculiarity of being a new, speedy, simple, powerful and non destructive technique.

In our work we have used a principal component analysis (PCA) of the chemical data, followed by a partial least squares regression to correlate the chemical-physical properties of the samples with quantitative measures. The main purpose of PCA is to extract the essential information contained in a large sample set and to decompose the data by finding combination of variables that best describe the main trend in the data set. The result of the PCA procedure is a decomposition of the spectral data matrix into principal components (PC) of scores (eigenvectors) and loading (numerical coefficients) vectors. The power of this method is that allow to describe the original data set using few principal components instead of the original variables with no significant loss of information. Also the original data set is decomposed in a structured part (PC) and a residual part composed essentially by noise and different information that is eliminated. Then, by means of a reference sample set, it is possible to extract a calibration line in order to carry out a quantitative investigation about the chemical and the physical properties of unknown samples.

Experimental

Polyamide fibers PAM 6.6 78/68 dtex with a disposition density of 11 thread/cm were disposed onto ten looms of 240 x 240 mm. The fibers were treated with different amounts of sizing agents (0, 2, 3, 3.7, 4.4, 4.6, 5, 5.9, 7.4, 9.4%) determined by laboratory titration. The fibers were sized using a sizing machine prototype developed by Giovanni Bozzetto SpA (Bg).

NIR spectra of the sized fibers were collected using a Bruker NIR Matrix-E spectrometer designed for on-line applications.

Spectra were obtained in reflection mode in the range of 10,000-4,000 cm^{-1} . A background spectrum were collected for each sample on Spectralone (a reference material with high reflectivity index nearly 99%) acquiring 32 background scanning counts. In the second step 10 spectra for each sample were collected using 100 scanning counts, 10 Khz scanning velocity and a resolution of 16 cm^{-1} . Data collection were performed using a Bruker Opus software, coupled with the Bruker Quant 2 software for multivariate analysis.

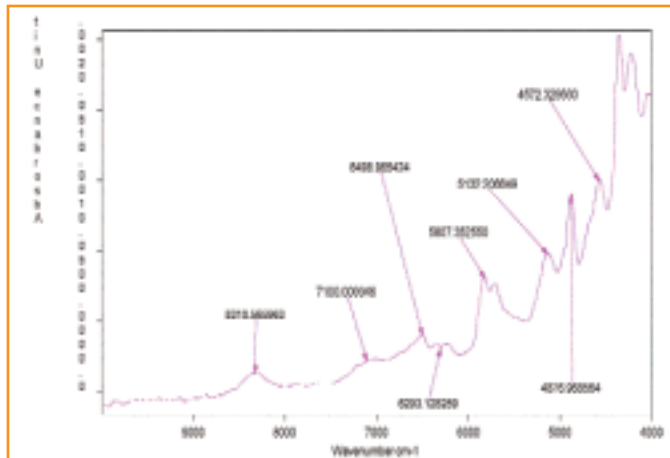


Figure 1 - Pattern of a polyamidic fiber; the principal absorption bands are indicated

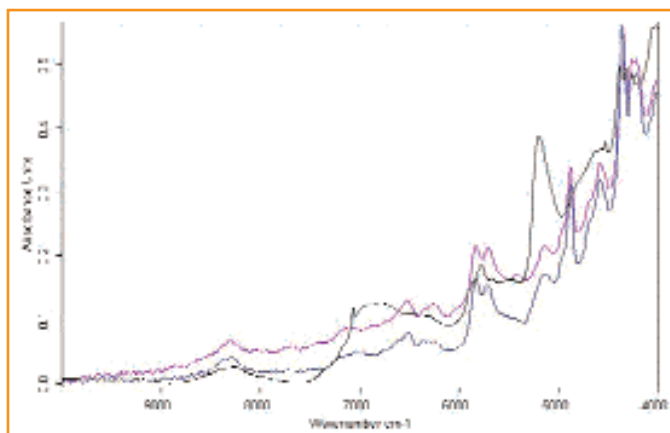


Figure 2 - Overlapping of the spectra acquired on two different sized fibers and the sizing agents spectrum

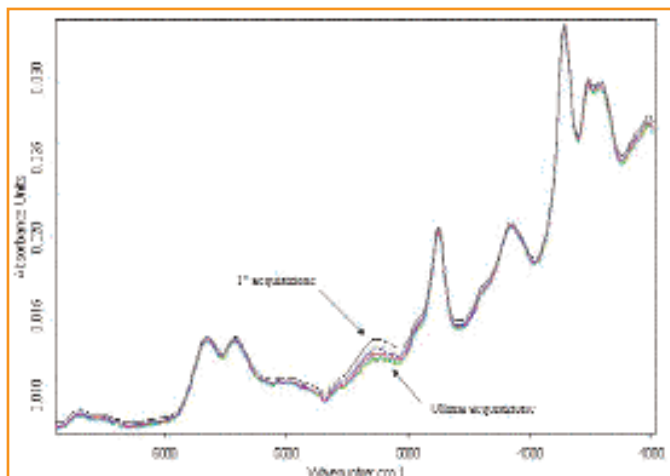


Figure 3 - Differences in absorption intensities between following acquisition on the same sample

Results and discussion

One of the main difficulty to apply the NIR spectroscopy in the quantitative analysis is the presence of broad and superimposed bands and the low absorption intensities. This can also be seen in the polyammidic fiber samples, as shown in Figure 1, where

the specimen of the loom samples is shown and the main absorption bands are indicated.

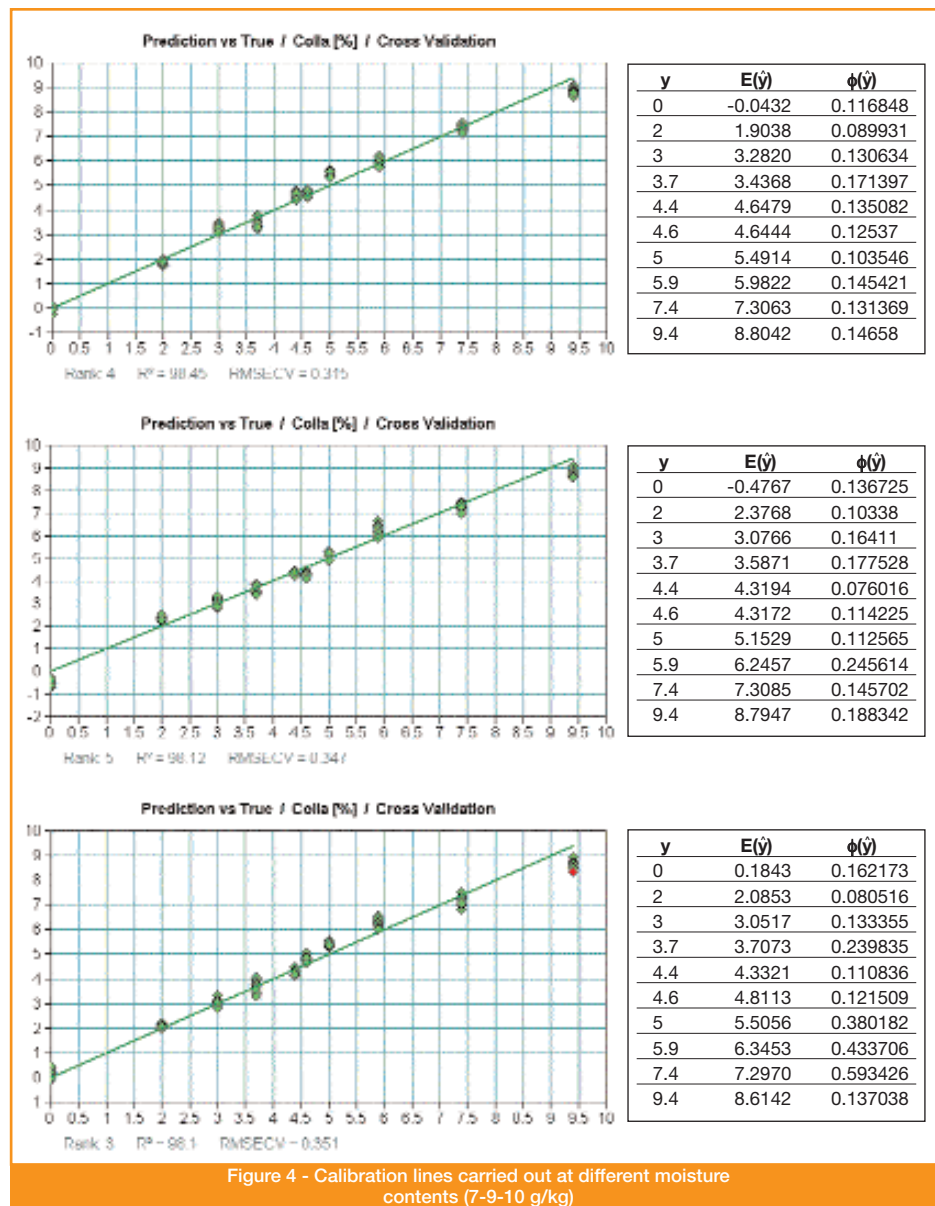
Since it is not significant to assign a definite absorption band for a specific bond vibration, the use of univariate calibration was excluded. Indeed, it is not possible in NIR spectroscopy to apply

the Lambert-Beer's law which expresses the direct correlation between the absorption intensities of a specific bond vibration and the compound concentration interested by the vibration; but is necessary, as previously mentioned, to carry out a multivariate calibration that analyses a wide absorption range and extract the principal information.

Figure 2 shows the spectra of the glue and sized fibers. As one can see, it is difficult to identify bands that can be ascribed to the glue only. Indeed, the presence of the absorption band of the O-H bond characteristic of the water and moisture [6] dominates the pattern. Moreover, because of intrinsic moisture in the fibers, as shown in Figure 3, a large variability of the intensity of the band at 5,100 cm^{-1} has found.

Thus, the atmospheric moisture and the presence of absorbed water into the fibers can compromise the repeatability of the measures, involving dramatic differences between patterns collected on the same sample.

Because the multivariate analysis extract the major information about the sizing content from the range between 6,100 and 4,600 cm^{-1} , that contains the water absorption band, this means that, for the calibration and the detection of the sizing quantity, we have to focus the attention on a wide absorption range affected by a



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repeatability problem due to the presence of water. To investigate this problem, different experiments in condition of controlled moisture were carried out. The samples were maintained for 24 hours in a conditioned chamber to have an intrinsic moisture content in equilibrium conditions. A set of measurements was performed for each loom in three different moisture conditions, respectively 7-9-10 g/kg of absolute humidity.

In Figure 4 and respective tables are shown the calibration lines and reported the average value $E(\hat{y})$ and respective standard deviations $\sigma(\hat{y})$ of the sizing values predicted by the chemiometric methods \hat{y} .

The calibration lines present a good prediction capability, in particular in the value range between 4 and 5% that is the characteristic sizing range of a real industrial production.

These measurements put into evidence the correlation between moisture content and quantity of sizing agents predicted by the chemiometric methods.

Indeed, if we validate the spectra collected at 9 and 10 g/kg of moisture conditions using the method performed at 7 g/kg, is clear that the method overvalue the sizing content, as shown in Figure 5.

This means that the chemiometric analysis does not only extract the exclusive information on the glue quantity, but the global information on the glue content together with the moisture. Thus it is mandatory to know the moisture conditions to obtain reliable values about the sizing agent content.

On the other hand, when the atmospheric moisture can be controlled and then considered in the chemiometric procedure (for data treatment) it is possible to achieve calibration diagrams that enable us to evaluate the content of the sizing agent in a reliable way.

After this first laboratory calibrations a series of on-line experiments at a sizing industry have been performed. The main problems are related to the non equilibrium moisture condition of the line; for this reason with the present experimental on-line condition is not possible to use the methods obtained in laboratory. Indeed, for the on-line development of this quality control technique is necessary a substantial reengineering of the production line to have stable condition near the measurement region to be

able to transport the laboratory methods to the line production directly; or alternatively it may be done a new calibration directly on-line, but this probably means larger investments.

Conclusions

In this work we have performed new chemiometric methods to evaluate the sizing agent content on polyamide fibers. The measures evidence a correlation between the glue percentage and the moisture content in the fibers; so it is impossible to have a distinctive information about the sizing agents content, but it is always correlated to the intrinsic water quantity. Also, to characterize this behaviour it was necessary a set of measurements in conditioned chamber that allowed us to predict a correlation between the glue content and the moisture. It is clear that it is necessary having stationary condition of the atmospheric moisture and the fiber in equilibrium with the ambient to have a good reproducibility on the measurements.

NIR spectroscopy coupled with chemiometric methods has demonstrated to be very suitable for on-line application due to his non-destructive nature; in the case of sizing industry we have demonstrated the prediction capacity of the method, but for on-line application it is necessary a reengineering of the production line to operate under conditions of controlled moisture.

Acknowledgements: The authors gratefully acknowledge P. Belloni of Bruker SpA for measurement support; G. Bernardi and A. Perico of Bozzetto SpA and Eng. Borsani of P. T. C. SpA for technical discussions.

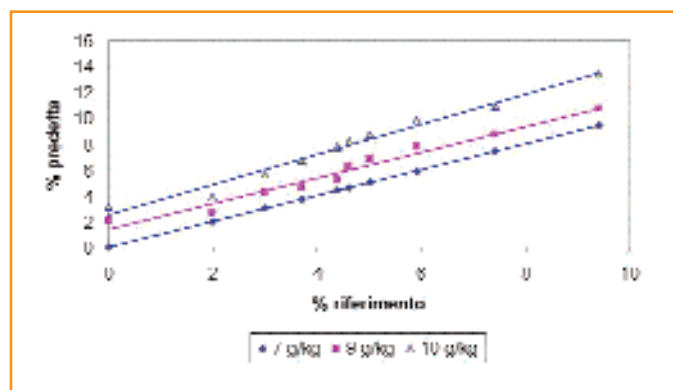


Figure 5 - Correlation between moisture content and sizing percentage predicted by the chemiometric methods

Applicazione della spettroscopia NIR per analisi quantitative nell'ambito dell'industria tessile

ABSTRACT 

Nell'articolo vengono discusse le potenzialità d'impiego della spettroscopia NIR per il controllo qualità "on-line" nel campo tessile. In particolare è presentata l'applicazione di metodi chemiometrici per l'estrazione di informazioni quantitative sulla percentuale di colla apposta su fibre sintetiche e viene discusso il ruolo critico dell'umidità nelle misurazioni "on-line".