

Quantitative determination of surface matter on natural fibres by Near Infrared Reflectance Spectroscopy

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Introduction

The near infrared region (NIR) is the part of the electromagnetic spectrum included between the visible region and the medium infrared region, i.e. between 13,000 and 4,000 cm^{-1} . All the absorption bands in the NIR region are the results of overtones or combination of overtones originating in the fundamental mid-range (4000-600 cm^{-1}) infrared region of the spectrum. The bonds involved are usually R-H (C-H, O-H, N-H, S-H, etc.) (1).

The NIR spectroscopy has become particularly important for the quantitative and qualitative analysis of different products in different field of application, including pharmaceutical, agricultural, petrochemical and textile.

In the quantitative approach the sample spectra evaluation by means of chemiometry can find a statistical connection between the spectral data and a known (by laboratory analysis) sample characteristic (2).

In the textile field NIR infrared spectroscopy has been found to be an useful technique to characterize raw materials, finished textile products and to control textile process. Because textile test specimens are in solid form, diffuse reflectance spectroscopy provides a special advantage by eliminating extensive sample preparation for testing textile materials such as fibre, yarn and fabric. NIR analysis is useful because a sample may be rapidly tested without destroying its integrity.

NIR has been used in the textile field to measure the percent moisture and finish-on-fibre of fibres and yarns, the amount of reducing sugars and maturity of cotton fibres, the degree of mercerisation of cotton fabrics, the percent polyester in polyester/cotton blends, the heat-set temperature of nylon carpets yarns, etc (3).

In this report we summarise two experimental works carried out at the Institute of Macromolecular Studies in Biella in collaboration with the Stazione Sperimentale per la Seta in Milano (Italy) concerning the determination of surface matter on natural fibres by Near Infrared Reflectance Spectroscopy. In both cases materials present on fibre surface at first stages of processing are determined because their influence on the characteristics and the behaviour of fibres in the following processing stages (e.g. dyeing, spinning, finishing).

The first work concern the quantitative determination of dichloromethane extractable matters on combed wool slivers which is a crucial analysis for the evaluation of combed sliver quality (4).

In the second work NIR spectroscopy was used to control the extent of degumming of silk fabrics, in a lab-scale model, which is the first step for an effective on-line control of degumming process (5).

Materials and Methods

Wool samples

Combed wool sliver samples were obtained from several wool combing mills in the industrial district of Biella in an attempt to obtain a comprehensive sample of local production. Wool samples used covered a wide set of samples of different origin, mean diameter, length, white degree and with DCM extractable matters ranging from 0.21% to 1.15 %.

Silk samples

Silk fabric samples with different extent of degumming loss (from 0 to 25% w/w) were prepared by the enzymatic degumming of different pieces of an undegummed silk fabric (crêpe, 79.6 g/m²). Two alkaline (3374-L and GC897-H) and one neutral (3273-C) protease were used in the laboratory degumming. Silk fabric samples of about 0.1 g were immersed in 20 ml of buffer solution (material-to-liquor ratio 1:200) containing different amounts of enzyme. Blank samples were obtained by treating silk with buffer alone, without enzyme. Enzymes were tested at different concentration (0.05-2 U/g fabric) and treatment time (5-240 min) and at fixed optimum pH and temperature. Degumming tests were carried out in a thermostatic bath under gentle shaking. Inactivation of proteases was made at 85°C for 10 min. At the end of the treatment, silk fabrics were rinsed with distilled water and dried at room temperature (6).

Fabric samples obtained were conditioned for at least 24 hours under standard conditions of temperature (20 °C) and relative humidity (65%) before NIR spectroscopy measurements.

DCM extractable matter

Residual grease content was obtained by soxhlet extraction using DCM according to IWTO-10-03, (7) paying particular attention to the accuracy of the analysis. Extraction times were held as close as possible to 3 hours, analytical grade solvent was used each time (no solvent was re-used). Some wool samples were deliberately under-scoured and others were re-scoured in combing mill in attempt to obtain a wide range of data. Each reference data was the mean of two determinations, each on 10 g of wool sliver.

Degumming loss

Degumming loss represents a quantitative evaluation of the degumming efficiency and it was measured as the weight loss of the fabric (expressed as a percentage of the initial weight) after degumming. Before weight measurement, samples were conditioned at 20 °C and 65% relative humidity for 24 hr.

NIR spectroscopy measurements

The NIR spectrophotometer used was a Perkin-Elmer FT-NIR System model Spectrum IdentiCheck with wavelength range 10000 to 3700 cm⁻¹ and 8 cm⁻¹ resolution. Sampling was performed in reflectance mode by means of the IdentiCheck Reflectance Accessory (ICRA) and spectra were collected as ratios against a BaSO₄ white standard background.

Each analytical spectrum was the result of the recording software combination of 32 scans.

For the measurements of DCM extractable matter on combed wool slivers, 2.0 g of wool (exactly weighed) were fixed to the 12 mm measurement round window by means of a 300 g steel plate as a dead weight that presses the fibre against the window, in a layer about 10 mm thick, using one measurement location.

For the measurement of degumming loss in silk samples, each sample, previously conditioned at 20 °C and 65% relative humidity for 24 hr, weighing around 0.1 g and measuring 3.5 x 2.0 cm, was folded and placed on the ICRA accessory and made to adhere with the pressure of a weight.

Single NIR spectra were acquired for both DCM extractable matter and degumming loss measurement and data were reduced by means of Spectrum Quant+ (Perkin-Elmer) software package supplied with the instrument. The DCM calibration spectra were not pre-treated in any way. The degumming loss calibration spectra were pre-treated with multiplicative scatter correction (MSC) to remove additive and scatter effects.

The PLS1 (Partial Least Squares1) algorithm was used for DCM extractable matter calibration and the PCR (Principal Component Regression) algorithm was used for degummin loss calibration. The data were associated to the spectra of the respective sample and a correlation between the samples measured characteristic and NIR spectrum was obtained.

The principal statistic used to assess the quality of the NIR results were the Coefficient of Determination (R^2) and the Standard Error of Prediction (SEP), that is the magnitude of error expected when independent samples are predicted using the model.

For validation purposes, different approaches were used for both determinations.

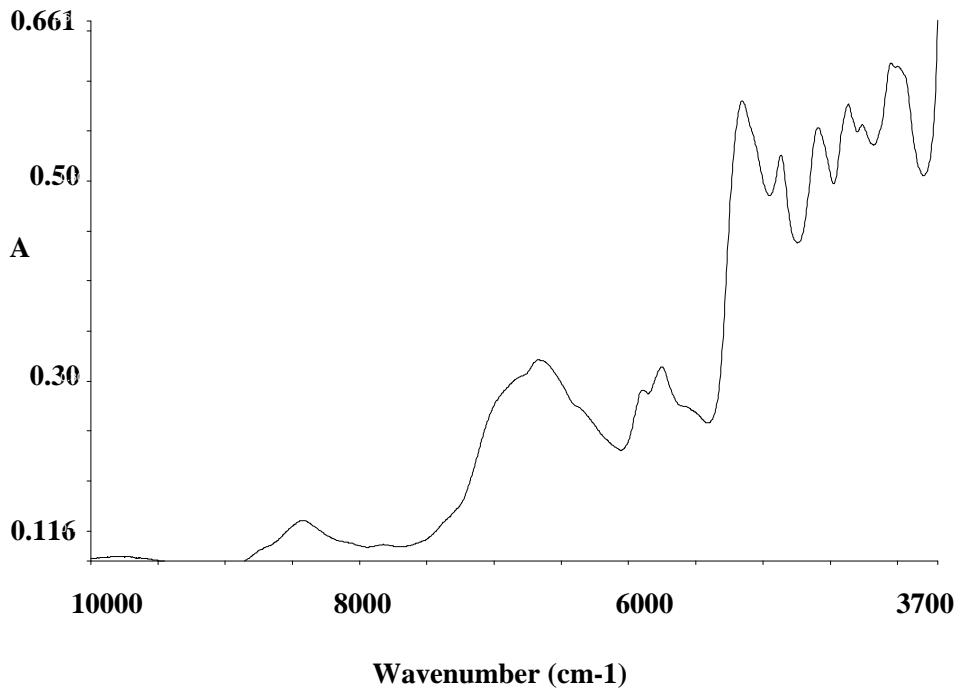
For DCM extractable matter determination, an independent and limited validation test was carried out on 13 commercial wool sliver samples from our quality control laboratory.

In the determination of degumming loss, for validation purposes 15 silk fabrics samples were removed randomly from the original samples. Calibration was made using the remaining samples. The set of 15 samples was used for the method validation and this process was repeated 20 times changing randomly each time the 15 samples used for calibration and validation. 300 predicted data of silk degumming were obtained and correlated with respective data obtained from degumming loss method.

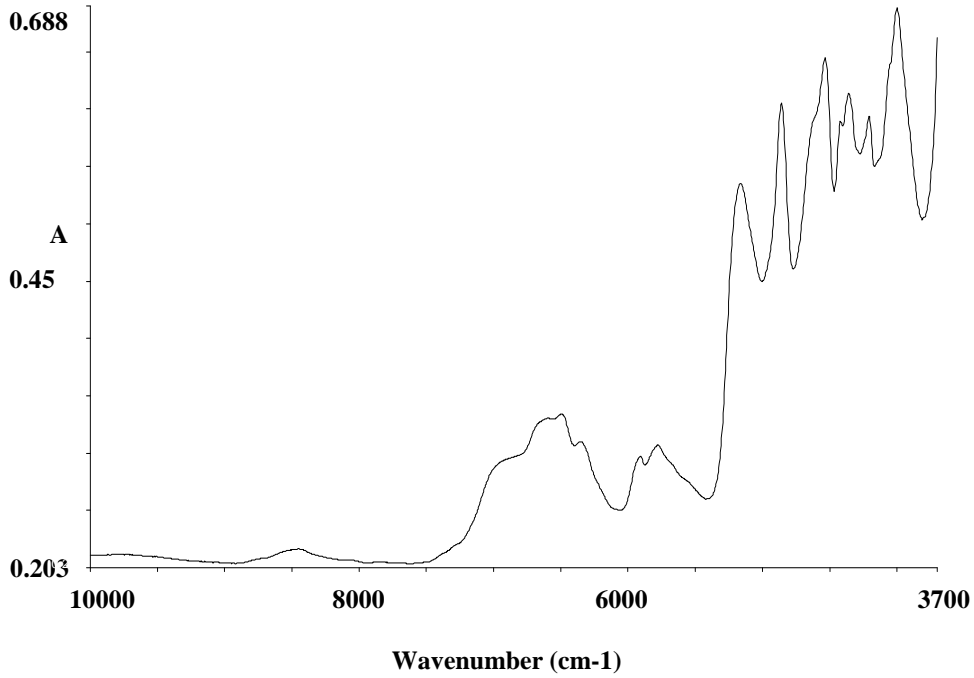
Results and Discussion

DCM soluble matter on combed wool slivers

Figure 1 shows the NIR spectra of a sample of wool (a) and a sample of silk (b). The shoulder at 7000 cm^{-1} is assigned to the first overtone of O-H stretching vibration of water and the band at 5200 cm^{-1} is assigned to a combination of the O-H stretch and H-O-H bending vibrations of hydroxyl group from water. The doublet at about 5800 cm^{-1} is the overtone of the C-H stretch of protein side chains and lipids. The bands between 5000 to 3700 cm^{-1} give information about the protein-type structure of wool and silk respectively.



(a)



(b)

Figure 1. NIR spectra of wool (a) and silk (b).

DCM extractable matter on combed wool sliver

After the industrial scouring processes, the wool fibres contain only limited quantities of DCM extractable substances, which are important for the commercial characterisation of combed wool sliver.

The spectra obtained from the same sample before and after the extraction with DCM are very similar, with wide bands poorly resolved and the changes associated with different residual grease values being very subtle. It is not possible to identify characteristic absorbances, which might be associated with absorption of extractable substances in DCM, which are a complex mixture of fat acids and superior alcohols, prevalently esterified.

The NIR spectra were analysed following the Spectrum Quant+ (Perkin Elmer Software) procedure.

For this purpose, 103 spectra were used as residual grease calibration set. The best results were obtained with the PLS1 (Partial Least Squares) algorithm, when considering the spectral region 9000-3800 cm^{-1} .

The correlation between DCM extractable matters according to IWTO-10-03 from the manual method and the corresponding instrumental results is shown in figure 2.

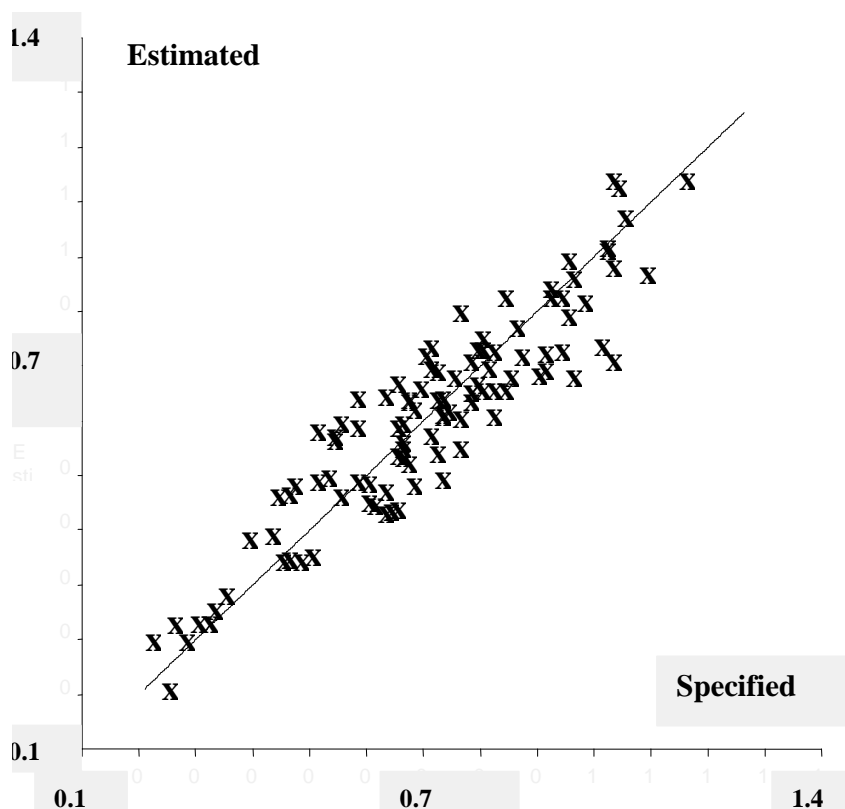


Figure 2. DCM extractable matter: NIR values estimated (y-axis) versus hand values specified (x-axis) – SEP= 0.1042 % w/w, M= 0.6963 % w/w, $R^2= 0.85$.

The standard error of prediction (SEP) obtained was 0.1042 % w/w for an average DCM extractable content of 0.6963 % w/w. The Coefficient of Determination (R^2) obtained was 0.85. Consideration based on SEP values in isolation is pointless because they must be compared with the standard error (SE) of the conventional soxhlet method used to obtain calibration sample data. Under normal circumstances, SEP cannot be smaller than the SE of the conventional method, considering that SE values are strictly correlated to the

number of determinations, to the control of the IWTO-10-03 application and skill of operators and laboratories. Trials on common materials can produce a population of results with SE ranging between 0.02 and 0.07 for residual grease calibration.

Results of validation, obtained measuring 13 commercial wool slivers using the correlation obtained, are shown in Figure 3.

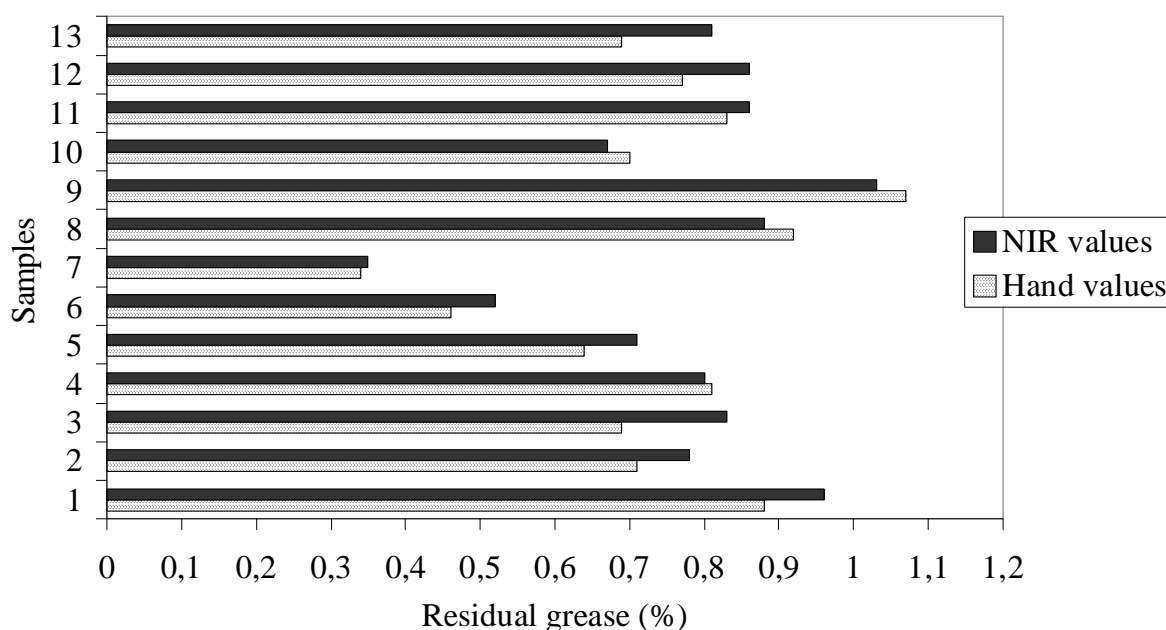


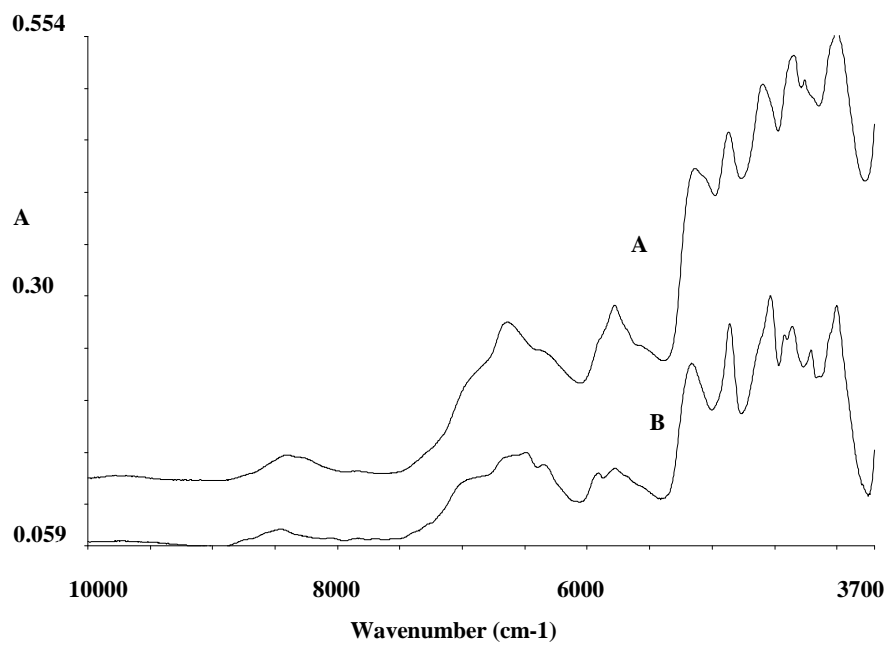
Figure 3. DCM extractable matter: NIR values predicted using the models obtained compared with hand values of some commercial wool tops.

Degumming loss on silk fabric

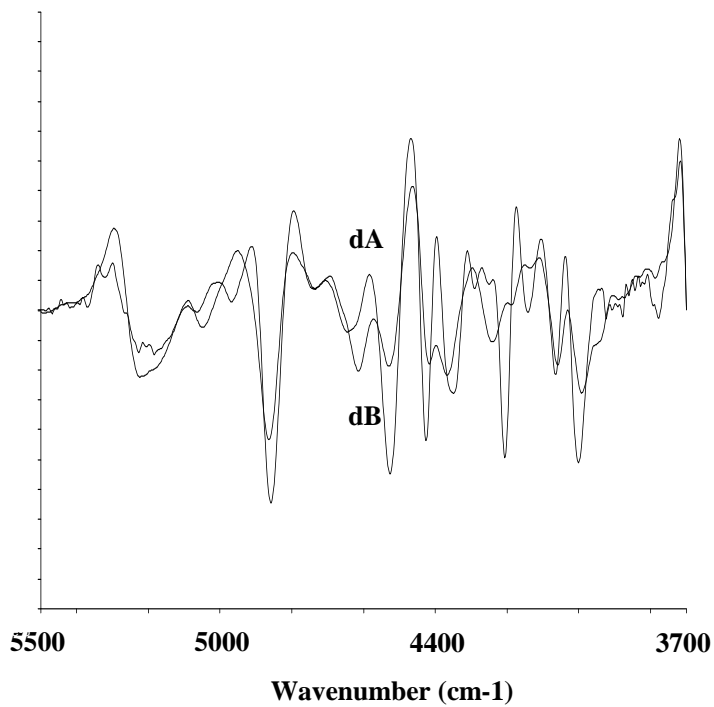
The silk filament spun by the silkworm is composed of two fibroin filaments held together by a cementing layer of sericin. The degumming process consists in removing the sericin layer from fibroin. This is a fundamental step in the silk processing cycle, which allow silk to gain the characteristic shiny aspect and soft handle that are highly appreciated by consumers.

Fibroin and sericin have different structure. The original spectra and the respective second derivative spectra of pure sericin (A) and fibroin (B) were shown in figure 4.

In original spectra the main differences between the two proteins, in the region between 5000 and 3700 cm^{-1} , are attributable to the different amino acid composition and characteristic molecular conformation (sheet structure). In order to obtain more resolution and so more structural information, the second derivate spectra of both spectra were obtained in the region between 5000-3700 cm^{-1} . After derivation, one strong band (4865 cm^{-1}), assignable to amide A-amide II combination, was observed in both sericin and fibroin spectrum. A partly broad feature assignable to the amide B-amide II combination at 4610 cm^{-1} was observed in each original spectrum. After derivation, NIR band separation at 4525 cm^{-1} was observed. This band was found in proteins rich in sheet structures and it is higher in fibroin than in sericin (8).



a)



b)

Figure 4 a) Original spectra of silk sericin (A) and fibroin (B). b) 2nd derivate spectra of sericin (dA) and fibroin (dB).

50 spectra of silk fabrics with different degumming loss were correlated with the weight loss of the respective samples (SE=0.312). PCR algorithm was used in the spectral region 10,000-3700 cm^{-1} . Figure 5 shows the correlation obtained.

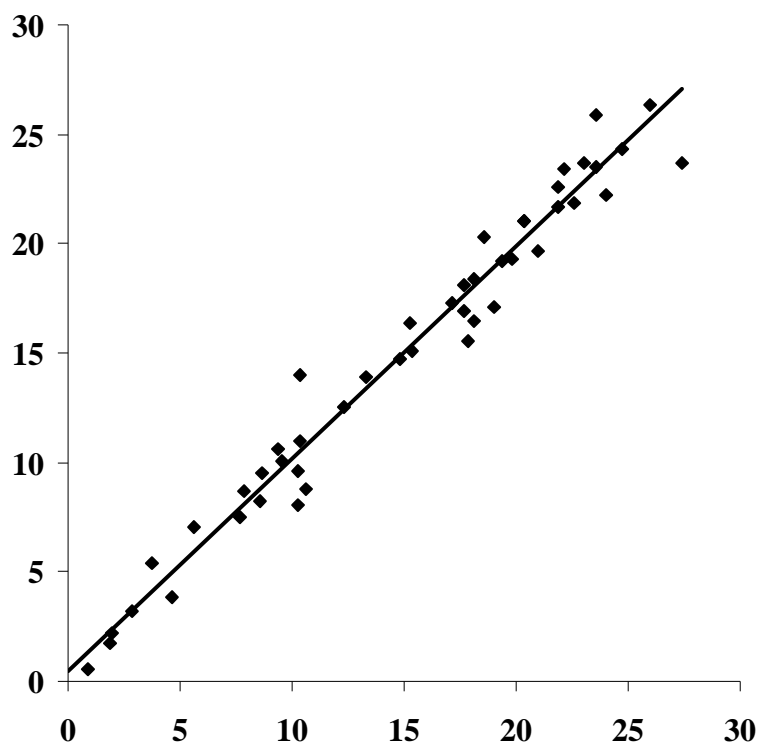


Figure 5. Degumming loss: NIR values estimated (y-axis) vs. values (x-axis): SEP = 1.6 g L^{-1} ; M = 14.6; $R^2 = 0.97$.

The NIR predicted results show a good correlation with reference degumming loss values, as shown by a coefficient of determination values (R^2) of 0.97 and a standard error of prediction of 1.6 for an average degumming loss of 14.6%.

From validation data, obtained from 300 predicted data of silk degumming which were correlated with respective data from degumming loss method, a $R^2 = 0.91$ was calculated.

Conclusion

In this paper two works were described, both concerning the determination of surface matter on natural fibres by Near Infrared Reflectance Spectroscopy.

In the first work NIR spectroscopy was used in a quality control of product, to assess the amount of the residual greasy matter on combed wool slivers. Greasy matter content on wool slivers can affect the spinning process, leading to sticking problems, if too high, or to fibre friction problems, if too low. It therefore has to be measured in order to know the amount of textile auxiliaries and spin finishes to be applied to the wool fibres for the subsequent processing stages. A correlation was obtained between amounts of solvent extractable matters determined using IWTO standard analysis with the NIR spectra of the respective samples. Results obtained have adequate quality for industrial implementation in combing mills. Actually in the industrial textile district of Biella, this determination method is used routinely or begins to be used in combing mills as quality control method.

In the second work NIR spectroscopy was used in the perspective of a process control, to determine the extent of degumming loss of silk fabrics. The correlation obtained using laboratory degummed samples, will be verified by means of tests performed at the industrial level, on true industrial samples of silk fabrics. Other perspectives, in the on line control of the silk process, are the NIR determination of sericin in the degumming baths (5) or the on line control of different process concerning the polymers grafting on silk fibroin.

References

1. E.W. Ciurczak in Handbook of Near-Infrared Analysis, Ed by D.A. Burns and E.W.Ciurczak, Marcel Dekker, New York, USA, p.7-11 (1992)
2. T. Næs, T. Isaksson, T. Fearn and T. Davies. Multivariate Calibration and Classification. Chichester, UK: NIR Publications; 2002
3. S. Ghosh, J. Rodgers in Handbook of Near-Infrared Analysis, Ed by D.A. Burns and E.W. Ciurczak, Marcel Dekker, New York, USA, p.495-526 (1992).
4. R. Innocenti, M. Zoccola J. Near Infrared Spectrosc., 11, 333-340 (2003).
5. R. Mossotti, R. Innocenti, M. Zoccola, A. Anghileri and G: Freddi. J. Near Infrared Spectroc. 14, 201-209, (2006),
6. G. Freddi, R. Mossotti, R. Innocenti, Journal of Biotechnology. 106, 101 (2003).
7. Method for the Determination of the Dichloromethane Soluble Matter in Combed Wool and Commercially Scoured or Carbonised Wool. International Wool Textile Organisation, 10-03 Specification (2003).
8. M. Miyazawa, M Sonoyama, J Near Infrared Spectrosc. 6, A253 (1998)