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FT-NIR Determination of the Content of Cotton in Blends with Viscose

Abstract

A spectroscopic method of determining cellulose content in cotton blends has been described. It is part of a wider project to develop spectroscopic methods of analysing textile blends. The method does not require using hazardous high-quality chemicals or time-consuming preparatory work and it reduces the time needed to determine the content to barely a few minutes.

Key words: cotton fibres, viscose fibres, NIR, quantitative analysis, fibre blends.

Introduction

Determining viscose content in blends with cotton is specified by Polish Standard PN-93/P-04847/05 "Textiles. Determining the fibre content in bicomponent blends using chemical methods. Determining the content of regenerated-cellulose fibres in blends with cotton using formic acid and zinc chloride." Many problems ensue from this method as it requires strict adherence to the specified conditions of the analysis, the quality of the reagents and the preparation procedures. The issue was thoroughly discussed by K. Mader, W. Lota and others [1]. Principally, regenerated-cellulose fibres from a blend are dissolved at 40 ± 20 °C for 2.5 hours in Marshall's reagent. That paper was the inspiration for this study, which is the result of an earlier analytical work on textile blends. Blends of regenerated cellulose and cotton were analysed using a spectroscopic method [2, 3]. The method and manner of examination are described along with the means of obtaining spectroscopic standards.

Experimental

Materials

The cotton fibres used were received from Edentex Sp. z o.o. (Poland), and viscose fibres of parameters 1.3 dtex/38 mm from Inatex, Sp z o.o., Zgierz, Poland. From these fibres were made the blends.

Results and discussion

For spectrophotometric examination of the textile blends, a Magna-IR 860 spectrophotometer was used, configured for near-infrared examination in the 10500 – 5500 cm^{-1} range, but limited by the measuring range of the InGaAs (Indium Gallium Arsenide) detector (Thermo-Nicolet, USA). A calcium fluoride beam splitter and halogen light source

were also used; the resolution was 8 cm^{-1} . In this method, the measuring beam has to be attenuated with a beam stop to ensure its optimum power for the detector. Placing and arranging a product or fibre blend in the measuring chamber is only meant to ensure even penetration of radiation through the fibres. Slight differences in their spatial distribution do not significantly affect the result of the examination.

Spectroscopic examination of a blend of regenerated-cellulose and cotton fibres is made by comparing the proportion of infrared absorption bands in the 10500 – 5500 cm^{-1} range, or a narrower one, depending on the level of noise and other disturbances [4, 5]. For assessing the composition correctly, the 9000 – 6000 cm^{-1} range is sufficient as it contains absorption bands from oscillating groups characteristic of the types of fibres in question. Radiation in the central range of near infrared, i.e. 12500 – 4000 cm^{-1} , as compared with visible light or mid-infrared, is much more penetrating and thus has less impact on matter. Therefore the amount of the sample placed in the measuring chamber for near-infrared measure-

ments can be up to several hundred times larger than the amount producing optimum spectra in mid-infrared. Furthermore optical effects (refraction, dispersion, reflection, interference, diffraction) do not disturb significantly the measuring beam within the sample.

An important parameter in spectroscopic measurements is the number of scans (single spectrum recordings). The level of random noise is inversely proportional to the square root of the number of averaged measurements. The duration of measurement does not translate proportionally into the quality thereof. The number of scans should be set individually depending on the accuracy requirements. In the useful range of radiation, the electric field of photons interferes with the overtone bands from the oscillating chemical groups. This produces wide and "smooth" absorption bands in the spectra, which are typical of near infrared. However, this does not preclude comparing and analysing the spectra [6].

The accuracy, or repeatability, of a single measurement can be verified by double measuring the spectrum of the sample:

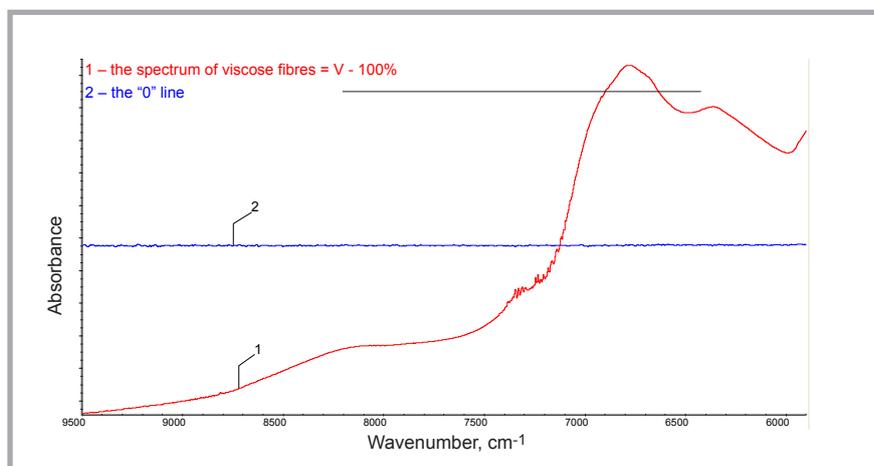


Figure 1. Spectrum of viscose fibres (1) and the "0" line (2) obtained after subtracting the spectra of the same sample recorded successively for 256 scans. Measurement deviation in relation to spectrum intensity is 0.8%.

as a reference background and measurement of the sample. The background is automatically subtracted from the actual measurement, giving a signal deviation from the theoretical value of "0" if both measurements were identical. As a result, this procedure provides information about the repeatability of the measurement and its impact on the quality of the analysis. An example of measuring the apparatus accuracy is shown in **Figure 1**. The resolution was 8 cm^{-1} , the number of scans 256 and the duration of measurement for these settings was about 3 minutes.

Accuracy can be improved by extending the duration of the measurement or changing the preparation of samples [7].

Taking those principles into account, a number of standards for blends of cotton and viscose can be measured so that they cover as wide a range of compositions as possible. The spectra of cotton, viscose and their blends are shown in the same scale in **Figure 2**.

The standard spectra shown in **Figure 2** reveal significant differences in their positions, which may be totally independent of the composition and weight of the blends. This makes it easier and faster to prepare the samples for measuring. In spectroscopic measurements of the composition of cotton-viscose blends, quantitative features of the spectrum are not relevant – such as absorption intensity, which is largely the result of attenuating the measurement beam with a beam stop, often having negative values. The only characteristic used to analyse the spectra is their shape, not the absorption values. To this end, all the spectra obtained are normalised to a 0 – 1 absorption range using OMNIC software. **Figure 3** shows these normalised spectra.

Once normalised, the spectra reveal characteristic features of their shapes that can be employed for quantitative distinctions between them. One such characteristic for cotton-viscose blends is a shift of the maximum in the $6800 - 6550\text{ cm}^{-1}$ range. As the near-infrared spectrum is recorded with a resolution of 8 cm^{-1} , it means that the measurement points are recorded at every 4 cm^{-1} with the software, automatically generating the averaged envelope for the points at every 1 cm^{-1} . Under these conditions, determining the band maximum is more accurate and can be also done outside the

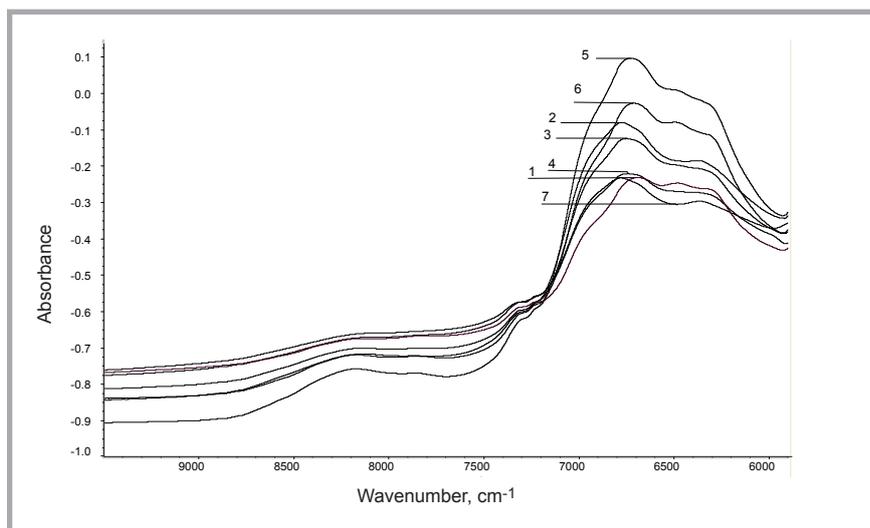


Figure 2. Standard spectra of cotton (C), viscose (V) and their blends; 1 - spectrum of cotton fibres = 100.0%; 2 - spectrum of blends: C = 14.1%, V = 85.9%; 3 - spectrum of blends: C = 38.6%, V = 61.0%; 4 - spectrum of blends: C = 44.0%, V = 56.0%; 5 - spectrum of blends: C = 64.0%, V = 36.0%; 6 - spectrum of blends: C = 82.8%, V = 17.2%; 7 - the spectrum of viscose fibres V = 100.0%

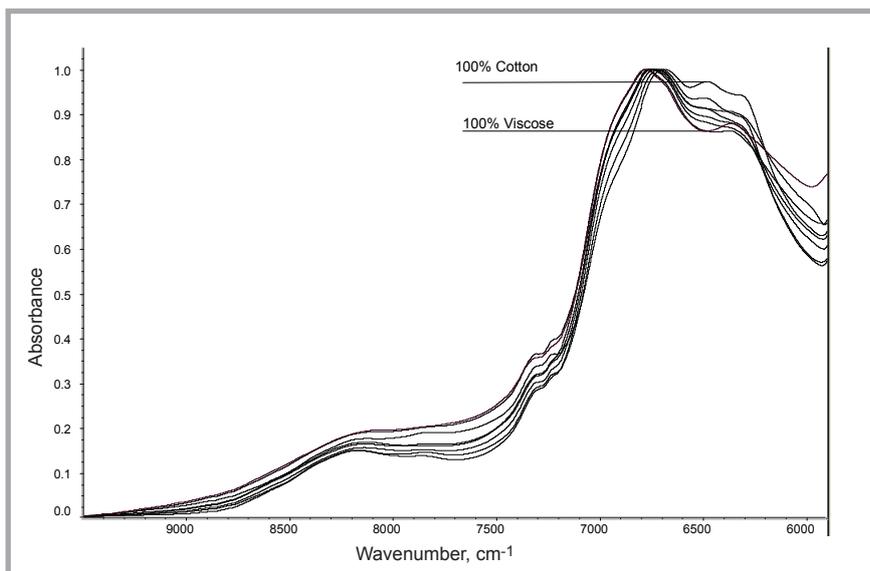


Figure 3. Spectra of cotton (C), viscose (V) and their blends normalised to a 0 – 1 absorption range.

measurement points. The accuracy (deviation of band maxima; **Figure 4**) for two measurements of the same sample taken in this experiment is 0.361 cm^{-1} . The shifts of the band maxima for the fibres of cotton, viscose and their blends are shown in **Figures 5** and **6** (see page 24).

One of the assumptions in this investigation was that several cotton-viscose blends should be prepared with known compositions and considerable heterogeneity of the spatial arrangement of their fibres to be subsequently used for obtaining standard spectra to determine the cotton/viscose ratio. Uneven distribution of fibres in real samples is natural. If this

effect caused significant differences in the results obtained, it would mean that the measurement method is defective. With the entire procedure taking about two hours, the R^2 coefficient of 0.984 is quite a good result. Once the correlation equation (**Equation 1**) has been worked out, determining the composition of cotton and viscose in a textile takes about 3 – 5 minutes. Calculating the composition (content) of cotton in a blend is done by inserting the value of the band maximum into the transformed linear correlation equation. For the above measurement and apparatus parameters, the equation will look like **Equation 2**:

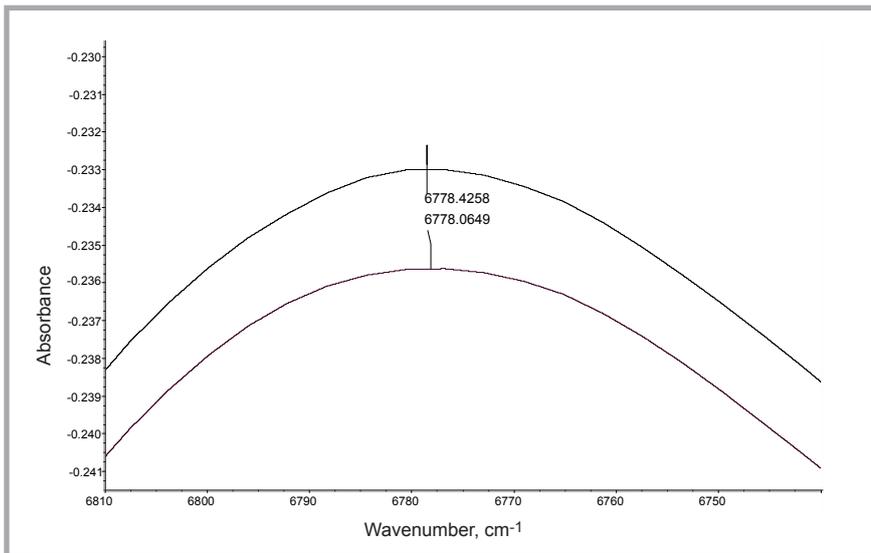


Figure 4. Band maxima for the same sample of viscose determined to three decimal places using OMNIC software.

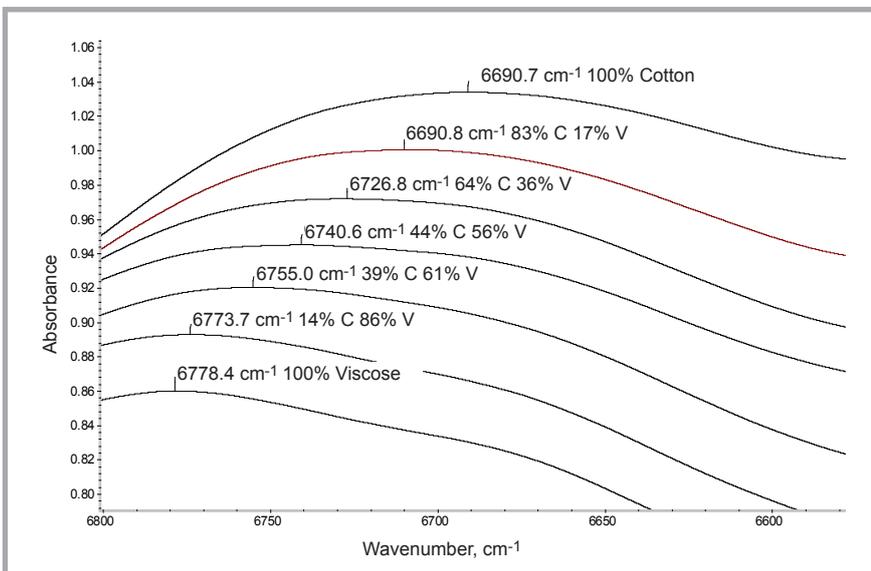


Figure 5. Comparison of the spectra of cotton, viscose and their blends in the 6800 – 6550 cm⁻¹ range indicating their compositions.

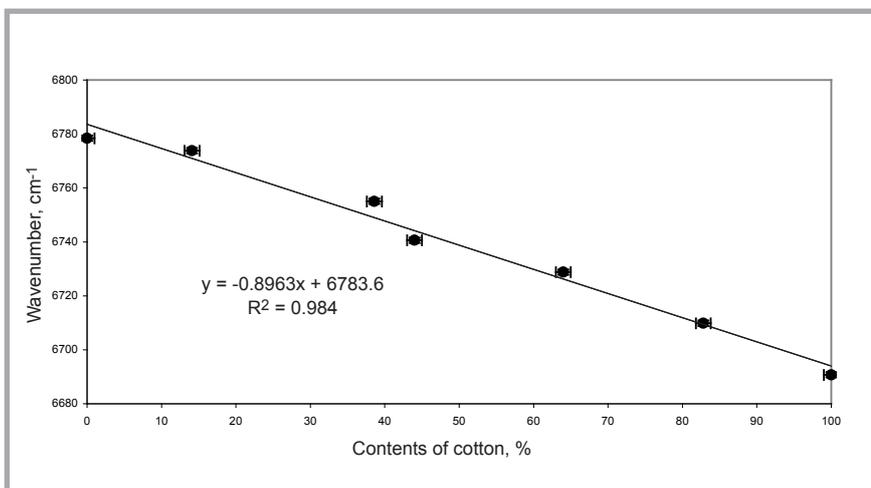


Figure 6. Comparison of spectral absorption band maxima in the 6800 – 6680 cm⁻¹ range for the spectra of cotton, viscose and their blends.

$$y = -0.8963x + 6783.6 \quad (1)$$

linear correlation equation

$$x = (6783.6 - y)/0.8963 \quad (2)$$

calculating the cotton content

where:

x - cotton content, in %,

y - band maximum wavenumber in the 6800 – 6680 cm⁻¹ range.

Alternatively the composition of cotton-viscose blends can be determined by creating a library of spectra. To this end, using the standard spectra of cotton and viscose fibre blends obtained earlier, simulated spectra are created for any viscose/cotton composition. The standard spectrum of cotton is assumed as the reference. Then using OMNIC software, the relative absorption coefficient for viscose/cotton must be set as follows:

- 1) recalculate the standards for cotton and viscose to a 0 – 1 absorption range;
- 2) multiply them by the percentage of each component in the standard blend;
- 3) select the relative absorption coefficient for viscose/cotton starting at 1.00;
- 4) add both spectra and recalculate the result to the 0 – 1 absorption range;
- 5) compare the simulated spectrum of the blend with the blend spectrum recorded on the spectrophotometer and recalculated to the 0 – 1 range. If deviations in the shape of both spectra are observed, go back to step 3 and adjust the relative absorption coefficient for viscose/cotton;
- 6) if the simulation result reflects adequately the similarity of both spectra, repeat the procedure for other compositions of standard blends.

As the penetration of infrared radiation through a fibre sample is related to partial absorption of certain wavelengths, their intensity decreases. Therefore the amount of radiation at a specific wavelength in the preparation may vary. Hence interaction with the components of the blend, whose proportions differ, is variable. The intensity of the absorption of each component is not directly proportional to their quantitative composition. This is proved by the varying coefficient of relative intensity of viscose absorption in relation to cotton in the spectra recorded and their simulations. To obtain the correct shape of simulated spectra for blends containing less viscose, its standard spectrum should be multiplied by a

greater coefficient of relative absorption. In other words, the higher the cotton content, the bigger shadow it casts on the viscose fibres, making them less visible. **Figure 7** shows the spectral coefficients determined for simulated spectra of standard blends along with an experimental trend line, its equation and the R² correlation coefficient.

Based on the experimental equation worked out as follows:

$$y = 9 \cdot 10^{-6}x^2 + 2 \cdot 10^{-4}x + 1.1199 \quad (3)$$

where:

x - cotton content, in %,

y - spectral viscose/cotton absorption coefficient,

The viscose/cotton absorption coefficient can be calculated for any composition of simulated blends.

Knowing the quantitative relations between viscose and cotton in the spectra of standard blends, one can embark on producing simulated spectra of blends with other viscose/cotton compositions. To this end, the standard spectra of cotton and viscose, recalculated to the 0 – 1 absorption range, should be multiplied by the assumed percentage composition, and the viscose spectrum should be further multiplied by the spectral coefficient from **Equation 3**. Then the spectra should be added and recalculated to the 0 – 1 range. A simulated spectrum of a viscose-cotton blend obtained in this way can be placed in OMNIC's library of spectra. The spectra of viscose-cotton blends simulated are shown in **Figure 8**.

With this library of simulated spectra, analysing the composition of any viscose-cotton blend takes hardly more time than is needed to place a product in the measuring beam, adjust the energy level for the InGaAs detector using the beam stop, take the measurement, recalculate it to the 0 – 1 absorption range and compare it with the library spectra. An example of this procedure is shown in **Figure 9**.

Comparative analysis shows the closest results, assuming a comparison range of 9000 – 5900 cm⁻¹, and the method of comparison based on the smallest differences of the first derivatives of the spectra, which can be done using OMNIC. This method indirectly eliminates some of the impact of the angle of spectrum's optical background. As the example

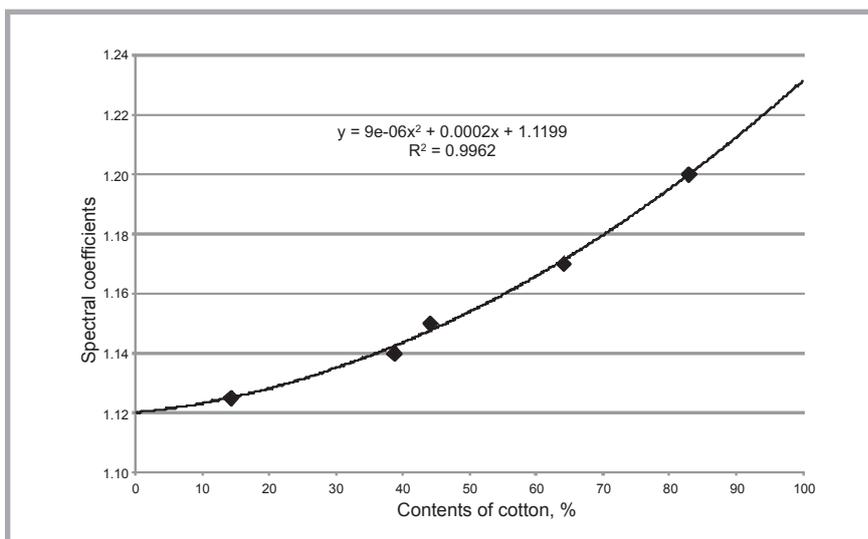


Figure 7. Viscose/cotton absorption coefficients determined for simulated spectra of standard viscose-cotton blends.

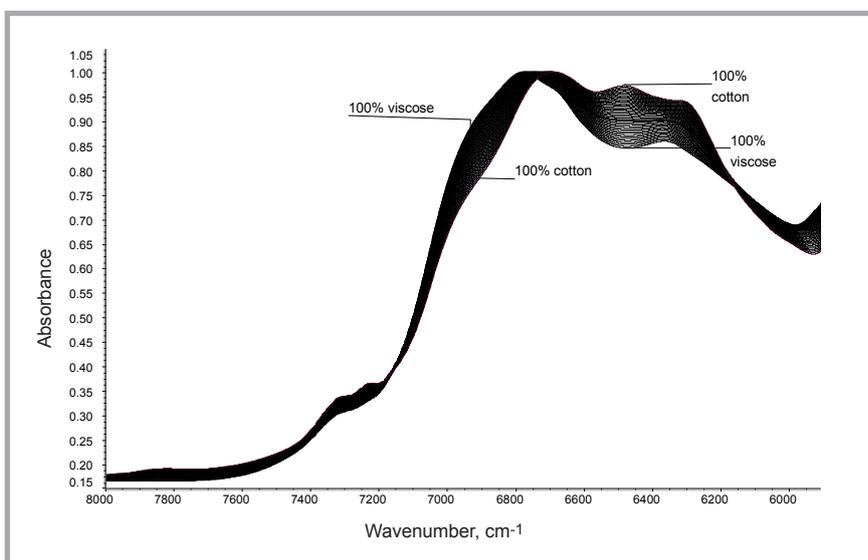


Figure 8. Simulated spectra of viscose-cotton blends produced for compositions at every 2.5% and spectra of 100% viscose and 100% cotton.

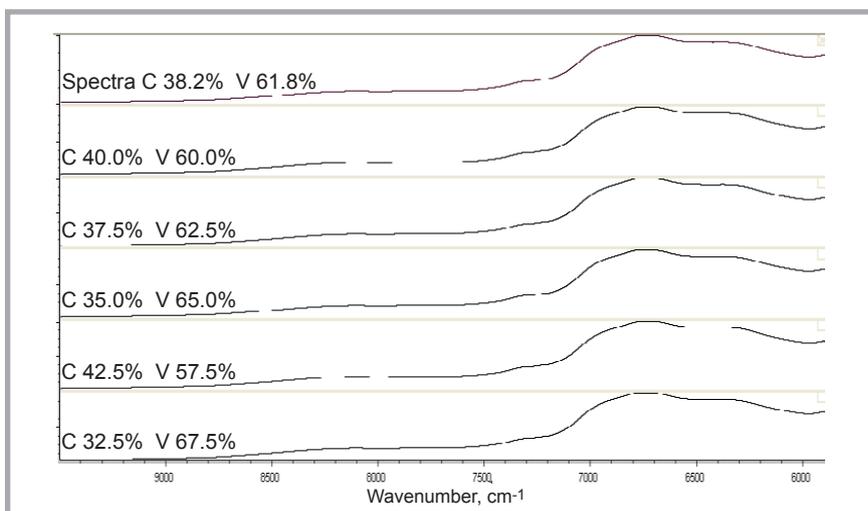


Figure 9. Spectrum of a blend containing 38.2% cotton and 61.8% viscose compared with the library of simulated spectra of viscose-cotton blends produced at every 2.5%.

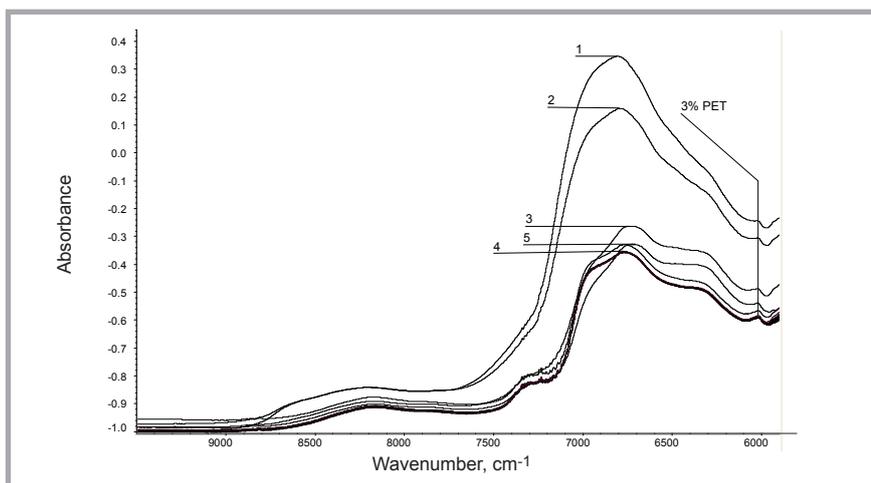


Figure 10. Spectra of a wet sample composed of 48.5% cotton, 48.5% viscose and 3% polyester during its drying and after cooling. 1 – spectrum of wet sample in temperature 30 °C; 2 – spectrum of wet sample in temperature 50 °C; 3 – spectrum of wet sample in temperature 70 °C; 4 – spectrum of sample stabilized at 150 °C after about 30 minutes four hours are insignificant; 5 – spectrum of sample after cooling to 40 °C.

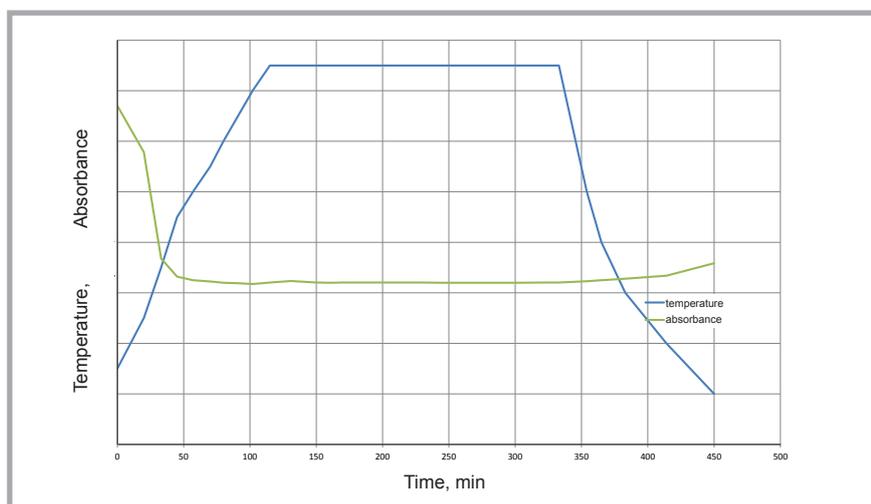


Figure 11. Changes in band intensity at about 6770 cm^{-1} during the drying and cooling of the sample.

shows, the result of this analysis is fast and satisfactory.

It should be remembered that the results of spectroscopic measurements in near infrared are affected by factors such as the colour of the fibres (for very dark or black colour, dye absorption can interfere with the measurement), impurities, humidity significantly different from that of the product under normal conditions, finishes, and other factors affecting the interaction of radiation and the sample. Many of these factors also affect the measurements obtained by other methods, including chemical ones. In order to eliminate random errors, it is advisable to compare the spectrum obtained by measurements with the simulated spectra from the library. This may give an answer to the possibility of the presence of other

fibres, significantly increased humidity of the sample, background resulting from the fibre colour, etc. The humidity of the sample can be quickly and easily removed by performing the measurements in a thermostatic sleeve. Heating the sleeve to 150 °C for about 30 minutes removes moisture and prevents rehydration, which may occur during examination by weight.

Because of their chemical structure, the humidity of hygroscopic fibres such as cotton and viscose varies considerably depending on temperature. **Figures 10 and 11** show an example of drying.

Figures 10 and 11 show an example of drying such samples directly in the measuring chamber, in an open thermostatic sleeve. Evaporating water can leave the sleeve freely with air convection. Mois-

ture from the air also has access to the sample during its cooling. Drying the sample requires high temperature and time. For this particular sample, band intensity is stabilised at 150 °C after about 30 minutes. The changes occurring over the next four hours are insignificant. Note the rapid moisturing of the fibres at lower temperature. The reactivity of the –OH groups and their ability to bind with water make the adsorption effects already visible at 100 °C. This fact should be taken into account in all the weight methods that involve drying the fibres, particularly hygroscopic ones.

Summary

The spectroscopic method of determining cotton content in blends with viscose has great analytical potential as it allows the composition of the blend to be controlled, providing quick and accurate results. After preparing the analytical method and library of spectra of blends, it is possible to measure cotton and viscose content in under a few minutes. The method is totally non-destructive to the materials measured. We can determine the content of cotton in the finished product we buy in a shop. This method was used to analyse the content of different fibres in their blends. It also enables the analysis of samples dried at high temperatures to prevent weight changes due to the high affinity of the fibres to water. Near-infrared spectra of the blends also reveal even small additions of other fibres, including polyester, as demonstrated in **Figure 10**.

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