Non-invasive analytical methods applied in the study of cultural heritage artefacts

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ABSTRACT – REZUMAT

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Ethnographic heritage textiles may be subject to risks generated in particular by various factors in close connection with the microclimate of the storage and exposure areas. In accordance with the current European trends of pest prevention and reduction and response to the infestation/contamination of the cultural heritage, the research direction of this study aimed at investigating the degradation of some women's clothing items, around 80–100 year-old, made of natural fibres, namely cotton. Throughout this paper, an essential aspect was taken into account for establishing a preventive or curative conservation strategy, namely the characterization of the fabric from which the three shirts are made. Thus, some physical and structural characteristics were determined by making use of different types of analyses: FTIR spectroscopy, the spectra specific for cotton; the microbiological analyses showed the presence of Bacillus subtilis and Rhizobium radiobacter, Staphylococcus aureus and Streptococcus pyogenes, which are not considered pathogenic or toxigenic to humans with the normal function of the immune system.

Keywords: *textiles, cultural heritage, non-invasive, conservation, fungi, FTIR*

Metode analitice non-invazive aplicate în studiul artefactelor din patrimoniul cultural

Textilele de patrimoniu etnografic pot fi supuse unor riscuri generate de diverși factori, care sunt în strânsă legătură cu microclimatul spaţiilor de depozitare și expunere. În conformitate cu tendințele europene actuale de prevenire și reducere a dăunătorilor și ca răspuns la contaminarea patrimoniului cultural, acest studiu vizează investigarea degradării unor articole de îmbrăcăminte cu o vechime de aproximativ 80-100 de ani, din fibre naturale de bumbac. În lucrare s-a ținut cont de un aspect esențial pentru stabilirea unei strategii de conservare preventivă sau curativă, și anume caracterizarea țesăturilor din care sunt confecționate cele trei cămăși. Astfel, au fost determinate unele caracteristici fizice și structurale, folosind diferite tipuri de analize: spectroscopie FTIR, spectre specifice fibrelor celulozice, tipice bumbacului; analizele microbiologice au evidențiat prezența Bacillus subtilis și Rhizobium radiobacter, Staphylococcus aureus și Streptococcus pyogenes, care nu sunt considerate patogeni sau toxigeni pentru persoanele cu sistem imunitar normal.

Cuvinte-cheie: *textile, patrimoniu cultural, non-invaziv, conservare, fungi, FTIR*

INTRODUCTION

Subject to the effects of globalization, some heritage items are stored or exhibited in museums, archives, libraries, archaeological sites, etc., and others have even disappeared or are at high risk in this regard. The conservation of cultural heritage, and the development of sustainable and innovative conservation techniques that do not affect the integrity of the item, all these are considered challenges to which interdisciplinary teams of specialists are subjected: preservationists, restorers, custodians, historians, archivists, biologists, chemists, physicists, geographers, ethnologists, bioinformaticians etc. [1, 2]. Textile heritage is the cultural expression of a nation through the social status of the holder as well as the regional and local characteristics transposed into the symbolism represented [3]. Heritage textile items, fabrics, yarn arrangement, and embroidery used in fabric making are tools for knowing the details of daily life in general, customs, values and behaviour of our ancestors. The restoration/ conservation actions and the strategies established to this end are based on studies and thorough analyses that provide information related to the characterization of textile materials [4]. Biological, physical and chemical factors, under the influence of anthropogenic activity and environmental factors, act in time, slowly or brutally, leading to the deterioration/biodeterioration of valuable items of the cultural heritage. The operation of this mechanism takes place within an open and dynamic system: human/artefact/environment. Microorganisms can contribute to

the deterioration/biodeterioration of artefacts, especially those made of natural threads (e.g., cotton), fibres with cellulose predominantly in their composition (about 94%), proteins 1.3% [5–6], being wrapped by a protective waxy cuticle. Also, the biological particles in aerosols (e.g., spores, toxins, allergens, etc.) present a potential risk not only to the heritage item but also to human health (visitors, users, curators, etc.). Identifying the type of fibres from which a heritage item is made sometimes allows for approximating the age of an artefact, the type of climate or trade routes and the manufacturing process used [7].

Literature review

Kavkler et al. [8] use the applications of Fourier-transform infrared spectroscopy (FTIR) to determine the degree of biodegradation of historical textiles stored in museums in Slovenia, especially those based on protein components compared to cellulosic ones. Thus, more intense biodegradation processes were underlined in the internal part of the fibres compared to their superficial part, these being caused both by microorganisms and other deterioration agents. Margariti et al. [9] support the use of FTIR microspectroscopy as a non-invasive and non-destructive technique in the study to preserve archaeological textiles. Peets et al. [10] prove that FTIR is a useful, non-invasive technique to identify textile fibres, discussing the advantages, but also some disadvantages. A range of spectra specific to different ranges of fibres is made available by the authors to those interested, in support in identifying the types of fibres.

Studies regarding the biodegradation of cultural heritage have been conducted by researchers such as Montegut et al. [11], Szostak-Kotowa [12], Abdel-Kareem [13], Arshad and Mujahid [14], Gutarowska et al. [15], Brzozowska et al. [16], Kumar and Shah [17], Sanders et al. [18], Trovão and Portugal [19], Unković et al. [20], Romero et al. [21] etc. In Romania, we mention the most recent research studies of different work groups, such as Radulescu et al. [22], Ilieș et al. [23–26], Marcu et al. [27], Bou-Belda et al. [28], Indrie et al. [29], Albu et al. [30], Wendt et al. [31], Gaceu et al. [32] etc.

MATERIALS AND METHODS

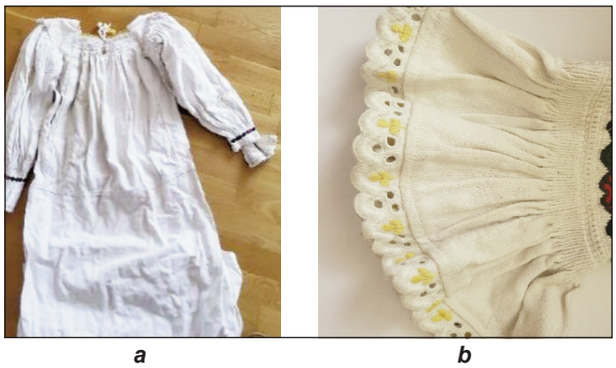
The study considered the analysis of two women's clothing items from Maramures County, Romania and a men's traditional cloth from Beius region, Romania, around 80–100 years old, made of cotton, belonging to private collections (figures 1, 2 and 3).

Both shirts originating from the Maramureș region are made of cotton cloth. They are large, both on the body and arms, which gives them a sense of greatness. They have long sleeves, up to the wrist.

Textile object no. 1 (figure 1, *a* and *b*) – Female shirt from Maramureș region. It has the size of the chest. When the shirt is dressed, a simple lower part named "stan" (figure 2, *a*) is added, or on special occasions, it has a richly decorated lower part (figure 2, *b*). Around the neck, it has a very wide lace with patterns of twigs, leaves and rose flowers, made of holes sewn on the edges called "fereşti". They have an angular appearance, resulting from broken lines and chained squares. Holes are achieved by cutting and hemming with the needle, by seaming on the threads. At the cuff, the sleeve is tightened through folds, but it widens towards the large-sized embroidery with floral patterns. The embroidery at the base of the neck (covering the cloth on the chest), from the shoulders and from the cuff is called "bezeri". Being stitched only at the top, they move in the wind and while walking. They are provided with two or three rows of holes, "fereşti". Folds are also present at the shoulders and chest area. All models have the colour of the canvas (white). The embroidery surrounds the neck, forming a zigzag called "șânguială". The cuffs have eight folds, four "scărițe" and two "suveici". The edges are provided with "boți" (thread nodes).

a *b*

Fig. 1. Object 1. Short traditional cloth, Romania: *a* – entire product; *b* – sample



a *b*

Fig. 2. Object 2. Long traditional cloth, Romania: *a* – entire product; *b* – sample

a *b*

Fig. 3. Object 3. Romanian traditional cloth, Beius area, Romania: *a* – entire product; *b* – sample

Buttons and loops present on the new shirt have been lost over time. Their traces are visible in the neck area.

Textile object no. 2 (figure 2, *a* and *b*) – Female shirt from Maramureș region. This shirt is complete, including the simple lower part named "stan". Around the neck, it is provided with very wide lacework, with no "bezeri" in the chest area. It has a closure system made of "guriță" and "chetori" (loops). The loops are provided with "ciucălăi" (also known as "ciucuri" (tassels) in certain ethnographic areas). They have two colours: white and the colour of the pumpkin flower. The pattern in the neck area is complex. We describe it from the bottom up: folds alternating with embroidery made of holes. Followed by "scărița măștcată" (big). Next, the layer of "suveicuțe", followed by "scărițe". Again, a layer of "suveicuțe", a layer of "scărițe", followed by another layer of "suveicuțe". Thus, there are three layers of "suveicuțe" separated by two layers of "scărițe". In the upper area, tusk-shaped pieces of cloth are sewn with a needle. Above we can see a layer of "pupi" (round ornaments) of different colours (white and the colour of the pumpkin flower). The pattern of the neck embroidery is called "formă într-un vârf și gaură" (shape in a tip and hole). The shoulder area presents small "bezeri" on a small pattern also in "formă într-un vârf și gaură". The pattern on the shoulders has a row of 'S' in a horizontal position, just like the interrupted and stylised "water stream" from the Dacian ceramics. At the cuff, the sleeve is tightened through folds, but it widens towards the small-sized embroidery with clover leaf patterns, and holes made with the tip of the spindle and sewn along the entire length of the circle. The narrowest part of the sleeve, at the cuff, is adorned with a chain of rhombuses. This type of rhombus is often found in Romanian folk art in and around the Carpathians, both in fabrics as well in wood hand-chiselling and carving. The rhombuses found on the cuffs are adorned with flowers made of double „grebluțe" (rakes), of different colours, framed by four folds, two layers of "scărițe" and "boți". The pattern in the neck area is highly adorned (folds, tusk-shaped items, "scărițe", "suveicuțe" etc.). The most complex patterns are present at the neck, shoulders and cuffs.

The object of the investigated patrimony (figure 3, *a*) is stored in an ethnographic museum in Romania. It is a men's shirt, dating about 80–100 years, from the area of Beius region, Romania. The men's shirt is an important piece of Romanian folk costume. It is a homemade cotton cloth and hand-woven. The shirt is cut much wider than the body and has a light puffy look. At the same time, the sleeves are wide. It has great robustness and vigour and does not bend easily on the body, it does not mould to it. The grandeur, sobriety, prestige and elegance are considerable advantages. In summer, it offers a cool atmosphere and in winter, the shirt is worn under other clothes, keeping a lot of warmth, because between its folds it retains real air cushions that have a thermal insulation effect. All the ornamentation of the garment is done by hand, sewn with a needle. The body of the shirt is crimped at the base of the neck. Above the wrinkle, a beautiful ornate collar is sewn. Its pattern, coloured in dark brown, is strongly geometrized by a series of squares (sometimes rhombuses) tied/coupled in the corners. At the bottom of the shirt, there is a simple hem. The wide sleeves are tightened at the wrist by a wrinkled cuff (sleeve, collar). The crease is similar to the shoulder, where the sleeve is attached to the body of the shirt. The simplicity of the shirt, especially specific to men's garments, with patterns of the same colour as the bottom (white) applied by sewing on the fabric and the additional presence of a single colour (dark brown), gives the shirt a special sobriety and beauty [49].

The study on how environmental conditions have left their mark on the type and characteristics of the textile material from which the two shirts has targeted two lines of research:

i) to determine the microbiological aspects associated with the clothing items analysed in the framework of the study it was aimed to determine the total number of bacteria, respectively the total number of fungi in the fabric. The microbiological tests were performed in the speciality laboratories at the Institute of Microbiology of the Republic of Uzbekistan. The working procedure was aimed at maintaining aseptic conditions and the following working methodology was used: the tests were carried out on the three samples specific to the two shirts originating from Maramureş and Beiuș regions (figure 1, *b*; figure 2, *b*; figure 3, *b*) made of cotton fabric. Samples from the textile samples surface (six) were collected using sterile cotton swabs [33, 34], on a surface of approximately 1 cm^2/ each sample. Cotton swabs were treated by immersion in one millilitre of sterile water. Three Petri plates measuring 90–100 mm in diameter were used for each sample. To determine the microbiological load, three culture media were used: Saline solution; Nutrient Agar (Himedia); Nutrient Sabureau medium (Himedia). If the colony growth was not noticed at a 1:10 dilution of the samples, the results should be considered as follows: 1 ml of the sample contains less than 10 bacteria.

ii) Fabrics are characterized by both their basic properties (flexibility, durability, etc.) and other characteristics that leave their mark on their appearance and behaviour under different conditions of use. The behaviour of the material under different environmental conditions is determined by the functional combination of the properties of the fabric and the characteristics and structure of the raw material. To highlight this fusion structure – type of material – behaviour, under different environmental conditions, we analysed some of the main general properties of the fabrics: structural properties and physical properties. The textile material from which the two shirts are made was subjected to several physical and structural tests, as follows:

1. Mesh density test was performed according to the European standard (EN ISO) 7211/2.

2. The thickness of the layer is a factor that affects the durability, permeability, fluidity and similar properties of the fabric being directly influenced by the diameter and number of threads in the textile material. The specific test for determining the thickness was carried out according to ASTM D1777.
3. Air permeability is a measure of the amount of airflow passing through a certain area of fabric at a certain time. The air permeability test was carried out according to ASTM D737-04 (2012).
4. Abrasion is the physical destruction of yarns, fibres and fabrics as a result of rubbing a textile surface against another surface. There is a close connection between abrasion and durability. Abrasion tests can contribute to the overall durability assessment.
5. Hygroscopicity is the property of fibres to accumulate and release water vapours in the atmosphere. Fibres retain a quantity of water that is influenced by their chemical composition and structure and the parameters of the microclimate to where they are stored or exposed. The hygroscopicity of the types of fibres influences the hygienic and comfort qualities of the textile garments and it is important to know the value to adjust to the technological processes and areas of use [35].

The samples were inserted in separate weighing vials, and placed openly in a water desiccator, where the relative humidity is predetermined at (98±1)%, and the time frame is 4h. After this time frame, they are closed and removed from the desiccator, and their weighing and drying are performed at a temperature of (107±2)°C (the drying temperature is (68±2)°C). After drying and cooling in a desiccator filled with dehydrated calcium chloride, the sample vials are weighed to constant mass using the analytical balance. The calculation formula used is:

$$H = (mB - mC) / mC \times 100\ (\%) \qquad (1)$$

where *mB* is the mass of the moistened elementary sample, in grams (g), and *mC* – mass of an elementary sample, after drying to constant mass, in grams (g).

Another indicator which characterises the mass of a unit area is the *areal density of fabric* (g/m^2). The recorded values of this indicator characterize the thickness of the warp and weft threads and the density of the fabric. Variations of this indicator can range on a fairly large scale of values, depending on the type of material, namely fluctuations which tend to increase the values of this indicator can be followed: after dressing up, printing, cutting, etc., as well as fluctuations which tend to decrease the values are recorded in cases of washing, bleaching, boiling, etc. of the fabric.

The determination of the fabric areal density: elementary samples are preliminarily conditioned to equilibrium humidity by keeping them under standard climatic conditions in an unstressed state, for at least 24 hours. In turn, each elementary sample is placed on a surface suitable for cutting, a metal template (cutter) is placed in the center, along which a square sample of 10 × 10 cm (or a round one with an area of 100 cm^2) is cut out. The elementary sample is weighed with an accuracy of ± 0.001 g while ensuring the safety of the threads. From the mass of the elementary sample, calculate the mass per unit area of tissue using the formula:

$$m_{oa} = m \times 100 \qquad (2)$$

where m_{oa} is the mass per unit area of fabric (per square meter) after conditioning under standard test climate conditions in g and *m* – the mass of the elementary sample in g.

In dry friction – initially, the dry sample is placed and set inside the tester. The second stage provides for the application of a strip of cotton material (about 50×50 mm) on the friction rod of the device, aiming for the friction surface to be smooth. The test must start on an elementary sample in one of the extreme positions of the rod, the device acting for 10 round trips, length of 100 mm, timing 10 s, and a load of 9 N. The tests are performed for the cotton cloth in wet and dry conditions. Thus, the material sample is immersed in distilled water (for 5 minutes); subsequently, squeezing is performed (the liquid content remaining in the cotton fabric is approximately equal to the weight of the adjacent cloth). The last stage of the test sets out to test the dry sample (GOST 9733.0-83 (Section 4)).

To identify the influence of the microclimate on the chemical properties of the textile material from which the three shirts originating from the Maramureş and Beiuș regions are made, we have collected samples taken from the three textile materials and analysed them, making use of the IR spectroscopy technique (FTIR). This technique is characterised by sensitivity, specificity and non-destructive nature, being minimally invasive. The application of FTIR for the analysis can be achieved for a fairly wide range of types of materials: e.g., historical fibres, paper, ceramic, etc. [36, 37]. FTIR test was done on the main components: the support textile fibre, very common when making old-time clothing items. Chemical changes can also be noted and even quantified, due to the ageing process of materials, especially those made of natural fibres, which is particularly important for the processes of conservation and restoration [38].

To analyse the type of fibre the chemical analysis of the efflorescence present on the sample was performed by infrared spectroscopy with a Miracle Accessory ZnSe S2PE infrared spectrometer (This ATR MIRacle Single Reflection Accessory includes the MIRacle base optics, a zinc selenide (ZnSe) crystal plate, a high-pressure clamp with three interchangeable tips, purge tubes, and a mount for the Spectrum Two spectrometer.

As for the *microbiological tests*, each fabric sample was processed as follows: for a weight of 0.7 g, 5 ml of saline was added. Next, they were placed under a magnetic stirrer for 30 minutes, leaving them for 3–4 hours at room temperature. 100 ml from each sample was added to the Petri plates with the nutrient

Agar. This was done evenly on the surface, using a spatula. Subsequently, the plates were incubated for 5 days at 37°C. Counting the bacterial colonies, grown on three plates, was achieved after an interval of 48 hours and 5 days, respectively. The mean value was identified as having multiplied by the dilution index and thus it was calculated the number of bacteria in 1 g of sample. The test was performed also using Petri plates with Sabouraud medium. The incubation of cultures was carried out at 20°C for 5 days. Counting the colonies of fungi and mould on three plates was carried out at the first stage of these types of tests with another culture medium; next, the number of fungi within 1 g of the sample was calculated by multiplying the mean value of the number of colonies by the dilution index.

RESULTS AND DISCUSSION

As for sample, object no 1 (MPA medium) – determination of the total number of germs revealed – 45 bacteria in 1 g of tissue; in the Sabouraud medium determination showed – 23 fungi in 1 g of tissue (GF XX1: 197).

When identifying samples of isolated cultures by MACLI-TOF mass spectrometry, using VITEK MS biometric analyzer, the following types of microorganisms were found: sample 1 (MPA) – bacterium *Bacillus subtilis*.

Object no. 2 sample: determination of the total number of germs showed 21 bacteria in 1 g of tissue, while in Sabouraud medium 23 fungi were determined in 1 g of tissue (GF XX1, part one page 197). When identifying culture samples isolated by MACLI-TOF mass spectrometry, using VITEK MS biometric analyzer, the bacterium – *Rhizobium radiobacter* was identified on the Sample, object 2 (MPA)

As for pathogenicity, the microbiological tests indicate the presence of *Bacillus subtilis* on sample object 1. This is a conditional pathogen, which can be often found in the dust; mainly it can be part of the normal microbiota of the human skin surface, and it is also found in the environment: in soil, dust, water and air. *Bacillus subtilis* is not considered pathogenic or toxigenic to humans with the normal function of the immune system, animals or plants [39]. On the sample object no. 2 – *Rhizobium radiobacter* was identified. A phytopathogen is known, and it represents conditional pathogenicity in people with intravascular devices suffering from immunodeficiency diseases [40, 41].

For the third object sample, Petri dishes with Sabouraud medium were used. The cultures were incubated for 5 days at a temperature of 20°C. After 5 days, the total number of fungi and mould colonies was counted on three plates, the mean value was found and multiplied by the dilution index and the number of fungi in 1 g of sample was calculated [50–52]. For the sample from (Sabouraud's medium) – 1,855 fungi in 1 g of tissue were calculated. For bacterial identification from cultures, we worked on VITEK® MS, an automated mass spectrometry microbial identification system that uses Matrix Assisted Laser Desorption Ionization Time-of-Flight (MALDI-TOF) technology. *Streptococcus pyogenes* has been identified but this species is not found in the list of microorganisms associated with the biodegradation of textiles mentioned by Pyzik [53]. If the clothing is worn, it should be borne in mind that the pH of the skin may change, which could lead to the exacerbation of pathogenic bacteria. *Staphylococcus aureus* and *Streptococcus pyogenes* [18].

Streptococci are gram-positive cocci hosted by humans and various animals. Streptococci are also present in the environment in dust, soil, air, and water. Most species are present in the normal flora in the respiratory tract, gastrointestinal tract, genitals and skin. Some species are pathogenic and can cause infectious diseases: erysipelas, impetigo, scarlet fever, rheumatism, cellulite, etc. Some studies show the possibility of transmitting bacteria such as

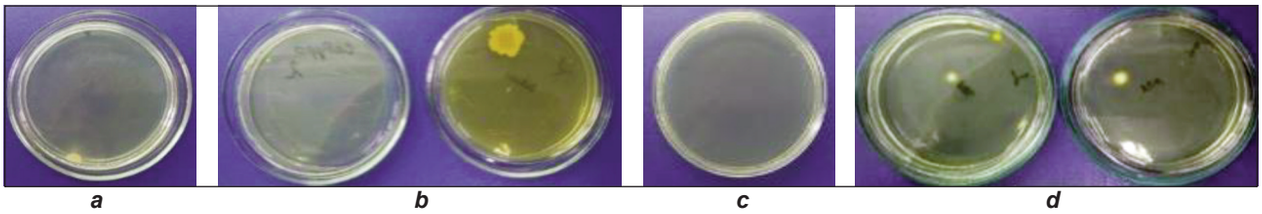


Fig. 4. The Petri plates different medium, a sample of textile object 1: *a* – Sample object 1 (MPA); *b* – Sample object 1 (Sabouraud); *c* – Sample object 1 (Sabouraud); *d* – Sample object 1 (MPA)

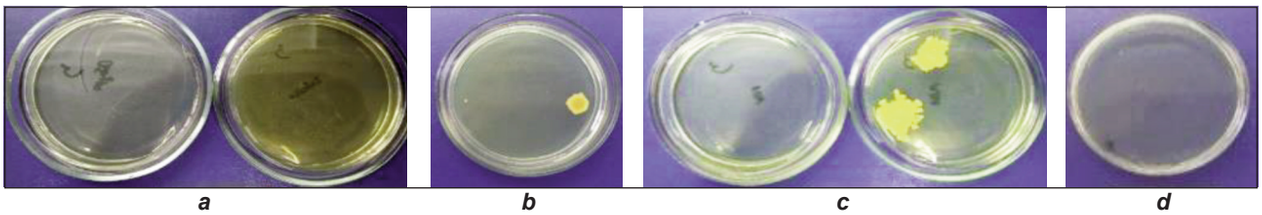
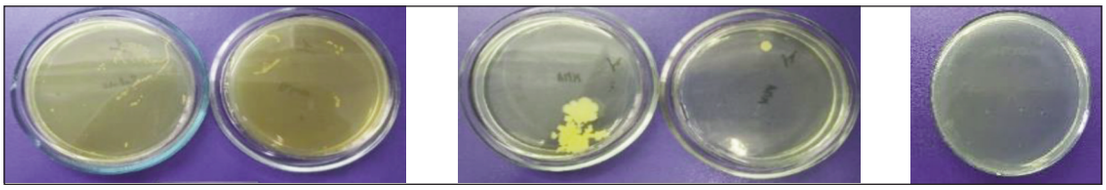


Fig. 5. The Petri plates, different medium, sample object no. 2: *a* – Sample object 2 (Sabouraud); *b* – Sample object 2 (Sabouraud); *c* – Sample object 2 (MPA); *d* – Sample object 2 (MPA)



a *b* *c*

Fig. 6. The genera of fungi, *Streptococcus pyogenes*, identified on the sample, in different medium: *a* – Sabureau medium; *b* – MPA medium; *c* – Saline medium

Table 1

INDICATORS VALUES (TEST DONE AT CENTEXUZ RESEARCH CENTER, UZBEKISTAN)				
№	**Indicators**	**Sample object 1**	**Sample object 2**	**Sample object 3**
1	Surface density (g/m^2)	318.2	348.4	326.5
2	Thickness (mm)	0.6	0.7	0.56
3	Air permeability (cm^2/cm^2.sec.)	54.8	21.8	53.6
4	Abrasion cycle	18000	21000	19500
5	Hygroscopicity (%)	11.01	11.26	11.62

Table 2

INDICATORS - COMPLEX OF TESTING LABORATORIES AT JV LLC "UZBEK-TURK TEST CENTER", UZBEKISTAN				
№	**Indicators**	**Sample object 1**	**Sample object 2**	**Sample object 3**
1	Breaking load (N)	513.8	602.4	567.9
2	Specific surface electrical resistance (Ω)	2.1 x 107	3.5 x 108	1.1 x 108
3	Colour fastness to washing (points)	-	4	-
4	Colour fastness to organic solvent (points)	-	4	-
5	Colour fastness to dry friction (points)	-	4	-

methicillin-resistant staphylococci, and gram-negative bacteria, including streptococci on clothes (white robes, uniforms-cuffs, seams on the waist, pockets) clothes that can represent a bacterial microdeposit and a channel of bacterial spread [54, 55]. For any person with natural immunity, the streptococci do not pose any danger [56, 57].

Identification of the influence that the environmental conditions have had on the structure of the textile material from which the two shirts are made, rendered by the same indicators which were evaluated at the Complex of testing laboratories at JV LLC "Uzbek-Turk Test Center", Uzbekistan, can be viewed in table 1 and table 2.

FTIR spectrometers. Fourier-transform infrared spectroscopy (FTIR) spectroscopy technique was chosen to characterize, especially from a physical point of view, the surface of the material and to give some clues regarding the degradation of the fibres. The FTIR spectra present specific cellulosic fibre peaks, typical for cotton (figures 7 and 8).

Fourier spectroscopy. With the help of Fourier spectrometers, the entire spectrum can be recorded simultaneously. Because in the interferometer an entrance opening of a larger size is permissible than the slit of spectral instruments with a dispersing element. Non-invasive and label-free Raman spectroscopy is an ideal analytical tool for fabric analysis non requiring sample homogenization. It is possible to extract the full range of chemical information without the need for biomolecular orientation, markers, stains or dyes. Unlike many other methods of analysis, such as Western blotting, gas chromatography/mass spectrometry, and time-of-flight mass spectrometry with laser ionization and desorption from a liquid matrix (MALDI-TOF).

FTIR spectra of both samples are showing similar bands and are presented in figures 7, 8 and 9.

The intense band at 3320 cm^{-1} is specific to the hydroxyl (O-H) groups corresponding to cellulose, lignin and water [42]. The 2890 cm^{-1} peak is associated with the stretching vibration of the C-H groups present in the composition of cellulose and hemicellulose [43], while the less intense peak at 1628 cm^{-1} can be correlated with the presence of O-H bending vibration of water from fibre [44]. The fact that the peak corresponding to the water is weak can be correlated with the age of the material. The presence of the sharp peak at 1740 cm^{-1} is characteristic of the carboxyl group from hemicellulose [45].

The 1426 cm^{-1} band is associated with the symmetrical bending of CH_2 groups in cellulose. The weak absorption bands between 1360 and 1300 cm^{-1} are

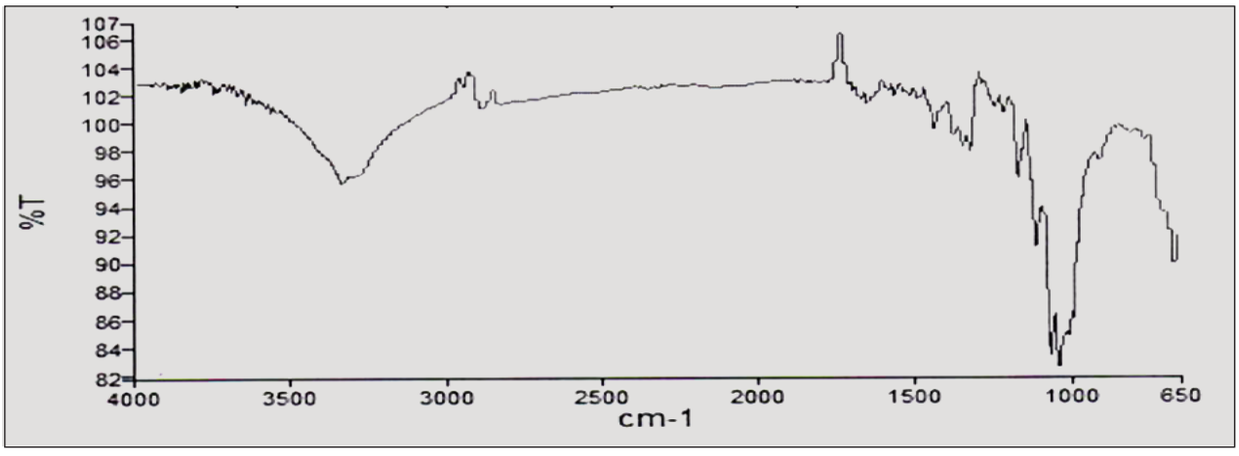


Fig. 7. FTIR-ATR spectra of cotton fibres, sample object no. 1

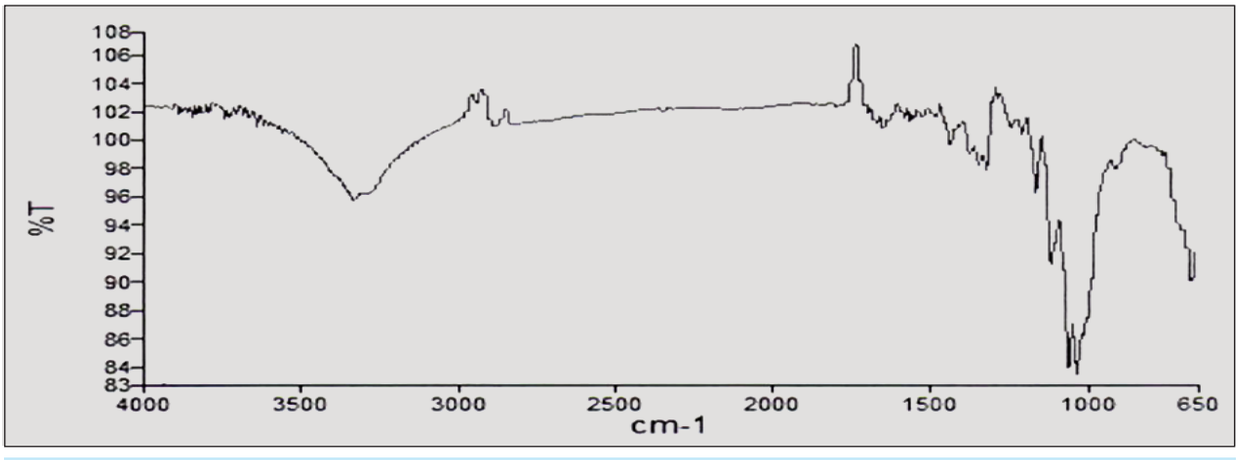


Fig. 8. FTIR-ATR spectra of cotton fibres, for sample object no. 2

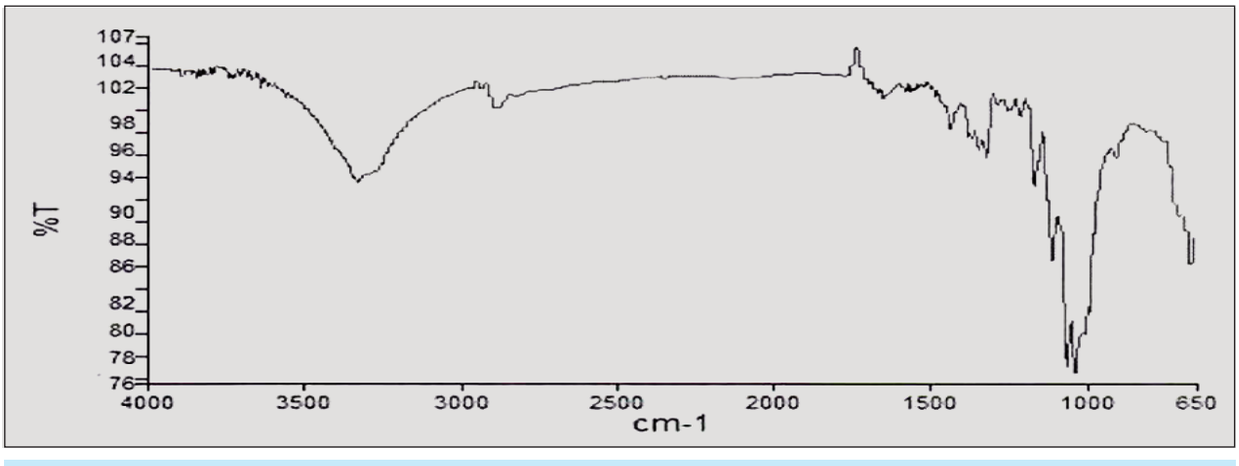


Fig. 9. FTIR-ATR spectra of cotton fibres, for sample object no. 3

due to the bending vibrations of the C-H and C-O groups in the rings of cellulose polysaccharides. The intense bands observed at 1030 cm^{-1} correspond to the stretching vibrations of (C-O) and (O-H) groups from cellulose polysaccharides. The weaker peak at 892 cm^{-1} indicates the existence of β-glycosidic bonds between monosaccharides [45].

At high wavenumbers, the broad and intense band appearing at 3325 cm^{-1} represents the hydroxyl (O-H) groups, specific to cellulose, lignin and water [42]. Further, at lower frequencies (2895 cm^{-1}) peak can be assigned with the stretching vibration of C-H groups of cellulose and hemicellulose [43].

The sharp band at 1745 cm^{-1} is assigned with the carboxyl group from hemicellulose [44]. The band at

Table 3

SPECTRAL ANALYSES ON THE INVESTIGATED SAMPLE				
Name (ID)	**Description**	**Search range**	**Libraries searched**	**Execution summary**
		Overlap	Library 1, polyatr, ATR Polymer Introductory Library, Library NDFIBS	
HitSpectrumID	**HitDescription**	**HitCorrelation**	**LibraryName**	**Library description**
F00352	FB352.SP FB352, SNOW FLAKE, COTTON, WONOCO, COPYRIGHT NICODOM 2007 IR- S	0.946613	NDFIBS	

Source: Analyses made complex of testing laboratories at JV LLC "Uzbek-Turk Test Center".

1628 cm^{-1} is assigned with the O-H bending vibration of water from fibre [45].

Considering the fingerprint region (less than 1500 cm^{-1}) the 1429 cm^{-1} peak is specific to the symmetrical bending of CH_2 groups in cellulose. Absorption bands seen in the 1365 and 1300 cm^{-1} region are characteristic of bending vibrations of the C-O and C-H groups of polysaccharides cellulose rings. Intense bands present at 1035 cm^{-1} are assigned with the (C-O) and (O-H) stretching vibrations from cellulose polysaccharides. At 890 cm^{-1}, the weaker peak shows the existence of β-glycosidic bonds between monosaccharides [44].

IR spectra recorded for reference samples (figures 7, 8 and 9) have absorption strips located in the frequency regions characteristic of cellulose [46–48]. From the analysis of the IR spectra recorded for the studied textiles, it is noted that the microclimate factors do not affect the molecular structure of the cellulosic chain, for any of the samples under analysis.

CONCLUSIONS

The different behaviour of the studied materials during the treatments can be explained by: the secondary, supramolecular and crystalline organisation of the cellulose, alternating amorphous and crystalline areas in the crystalline structure of the cellulose, the presence of microscopic and submicroscopic voids in the structure of the fibres, as well as the presence of the other main chemical components – hemicelluloses and lignin – in the structure of textile fibres. FTIR spectroscopy applications on biodegraded historical textiles is a successful non-invasive technique which can underline the fabric decay caused by microorganisms, but also by other deterioration agents. At the microbiological tests, the bacteria species *Bacillus subtilis* and *Rhizobium radiobacter* were isolated and identified, being the main part of the normal microbiota of the human skin surface, and they are not dangerous to a person with the normal function of the immune system and its presence can be also in the environment: in soil, dust, water and air. The strategies and tools used for investigations (microbiological etc.) of cultural heritage objects are not standardized, being in continuous development, each with advantages and disadvantages depending on the type and purpose of the study, but especially on the available infrastructure [2, 58–62]. If the clothing is worn, it should be borne in mind that the pH of the skin may change, which could lead to the exacerbation of pathogenic bacteria. *Staphylococcus aureus* and *Streptococcus pyogenes* [54].

Insights: New/unconventional methods of protection are necessary to be identified and tested against the influence of microclimate conditions in the ageing processes of cellulosic materials from ethnographic textile collections. In the context of future research, we will be taken into account the study on the effects of the main microclimate factors (temperature, humidity, lighting, etc.) on the permanence and durability characteristics of textiles made of cellulosic materials. Their action on natural pigments will also be analysed, using other investigation techniques such as High-performance liquid chromatography, SEM analysis etc.

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