# Spectral Study on Plant Extracts Releasing from Medical Fur Items

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*The objective is to obtain leathers and furs for medical or everyday use, with high performance characteristics, through the use of new plant extracts that have not been used in leather industry so far, as an alternative to the use of chemicals with pollutant potential. Developing a complex analytical system for the characterization of natural extracts as additives and their role of fur and leather processing, is important both scientifically and technologically. The complex system consists of two spectral methods coupled and interdependent spectroscopy in the ultraviolet and visible (UV-VIS) and infrared spectroscopy with attenuated total reflection (FT/IR-ATR). For the spectral study of releasing kinetics of volatile substances, from the hair of natural furs processed for medical use, a series of oil extracts from the following plants have been selected: thyme, lavender and sage. For this purpose, desorption rates of active principles in fur supports treated by spray coating or by immersion have been analyzed and a series of fur items have been created, which can be treated with plant extracts to achieve prophylactic effects (bactericidal, anti-inflammatory, revulsive, relaxing etc).*

*Keywords: spectral kinetic study, natural extracts, additives, leather industry, ecological items*

The plants have a lot of effects [1-7] due to their chemical composition which includes a large variety of compounds, such as:

•*Thyme (Thymus serpyllum)* contains volatile oils such as: carvacrol, cymol, $x_1$-pinen, 1-borneol, linalool, as well as over 10% tannin with bactericidal, antioxidative and tonic effects.

•*Sage (Salvia officinalis)* contains volatile oil with a composition of: thujon, alpha and beta pinene, camphor, borneol, cineol as well as: tannin, oleaonic acid, sitosterols, estrogenic substances, nitre, bitter principle (picrosalvine), niacin, caffeic acid, fumaric acid, resins, vitamins $B_1$ and C, potassium salts. Sage has bactericidal, sedative, anti-thermal, tonic, anti-inflammatory, antispastic, antiseptic, antisudorific and antioxidant properties.

•*Lavender (Lavandula angustifolia)* contains volatile oil with: 44-50% linalil acetate, linalil butyrate, geraniol, free linalool, linal valerianate, borneol, coumarin, ethyl-n-amyl ketone, nerol, furfurol, a-pinen, cariophylene, acids and esters, tannin, bitter principles, mineral substances, flavones etc. The main properties of lavender oil extract are: antioxidant, bactericidal, antispastic, calming, analgesic and relaxing.

## Experimental part

Blend of volatile oil extracts in ethylic alcohol has been used to treat medical furskins by spraying or by immersion for 10 minutes. Selection of plant extract combinations was based on organoleptic assessment of smell persistence in time and profilatic properties. Two types of fur samples treated by spraying with blends of volatile extract oils have been created: LSB (based on lavender and sage extract oils ) and CSB (based on thyme and sage extract oils) which have been sealed in plastic foils (1) or have been left as such (2). Other range of fur samples were treated by immersion in the same blends of volatile extract oils and marked with (3) for those sealed in plastic foils and (4) for those left as such.

Plant extracts released from medical furskins were prepared by aqueous maceration. The extracts were allowed to settle for 6 days at 15$^{o}$C, the obtained solutions were filtered and subject to tests for physico-chemical characterization by UV-VIS spectra. In view of selecting variants with persistence of volatile components, a kinetics study of release in time was conducted based on identification of flavonoid components by means of UV-VIS and FT/IR-ATR spectrometry. Analyzed samples were: sage oil extract, lavender oil extract, thyme oil extract, untreated medical fur (control), treated furs by spraying and stored in free state (LSB1, CSB1), treated furs by spraying and stored in sealed state (LSB2, CSB1), treated furs by immersion and stored in free state (LSB3, CSB3) and treated furs by immersion and stored in sealed state (LSB4, CSB4).

A UV-VIS spectrophotometry study of leach kinetics of plant extracts from treated furs was carried out for 9 days, in saline solutions of NaCl 0.01%, *p*H=5. 06 until reaching a constant speed of active substances release [8].

The study was done for similar conditions to in vitro release, at the temperature or 37$^{o}$C, since furs will be used as insoles for medical or everyday use. Insoles with immobilized vegetable extracts have the role of reducing sole sweat and of creating comfortable, anti-inflammatory, bactericidal and good thermal effects. The effect of adding vegetable extracts on structural properties of furs was studied compared to a control fur: release of biologically active substances from furs and surface characteristics. Samples analyzed–furs with and without immobilized vegetable extracts have surfaces of 1cm$^2$ and identical thicknesses to the control. Samples have been immersed in the same quantity of distilled water with NaCl (c=0.01 %), of 30 cm$^3$. UV-VIS spectra have been done, for 9 days

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| fur sample | $T_I$ | $T_{II}$ | $T_I/T_{II}$ | $T_{OH}$ | $T_{OH}/T_I$ | $\Delta\nu = \nu_{T_I} - \nu_{T_{II}}$ (cm$^{-1}$) | $T_{C=O}$ | $T_{C=O}/T_I$ | $\nu_{C=O}$ (cm$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| LSB1 | 98.5802 | 97.478 | 1,011 | - | - | $\Delta\nu$= 1692.23 cm$^{-1}$ – 1515.78 cm$^{-1}$ = 176.45cm$^{-1}$ | - | - | - |
| CSB1 | - | - | - | - | - | - | 99.88 | | 1703.8 |
| control sample | - | - | - | - | - | - | - | - | - |
| LSB3 | 98,816 | 99,42 | 0,99 | 99,20 | 1,003 | $\Delta\nu$= 1644.98 cm$^{-1}$ – 1517.7 cm$^{-1}$ = 127,28 cm$^{-1}$ | - | - | - |
| CSB3 | 96,922 | 96,97 | 0,99 | 98,43 | 1.015 | $\Delta\nu$= 1629.55 cm$^{-1}$ – 1517.7 cm$^{-1}$ = 111,8 cm$^{-1}$ | 98,14 | 1,01 | 1741,4 |

**Table 1**
FT/IR-ATR SPECTRAL CHARACTERISTICS OF FUR SAMPLES WITH AND WITHOUT IMMOBILIZED VEGETABLE EXTRACTS (BY SPRAY COATING AND IMMERSION)

and at fixed wavelengths (characteristic to specific peaks) and absorbance values have been read. Release peaks from analyzed samples in the saline aqueous solution have been identified for a period of time. From experimental curves, release rates of immobilized bioactive principles could be determined over time. UV-VIS fingerprint spectra have been done for vegetable extracts to be immobilized in furs and specific peaks have been identified.

## Results and discussions

*FT/IR-ATR spectral analysis*

The method is sensitive for identification of volatile substances [1], therefore samples with higher concentrations of volatiles have been chosen. Four furs samples treated with volatile oil extracts (LSB1, CSB1, LSB3, CSB3) have been analyzed by FT/IR-ATR spectral absorption technique for the purpose of identifying possible chemical bonds between plant extract components and keratin.

Knowing absorbance (and transmittance) at each absorption band, the following ratios have been calculated:

- $T_I/T_{II}$ (amide I/amide II) ratio whose value provides information on the hydrolysis degree of the support;
- the difference between wavelength numbers specific to amide structures ($\Delta\nu$) which provides information on denaturation;
- $T_{OH}/T_I$ ratio whose value provides information on the hydrolysis degree of the chain;
- the presence of a band at $\nu$ =1700–1750 cm$^{-1}$ indicates the carbonyl/carboxyl structures.

Experimental data registered in transmission for fur samples are given in table 1.

Experimental results for the four analyzed samples in comparison with control sample confirm the following:

- the 4000–3200 cm$^{-1}$ domain is attributed to elongation variations: O-H and N-H, present for all analyzed samples;
- the 2500–2000 cm$^{-1}$ domain: the literature indicates the presence of elongation vibrations given by groups such as: Xa≡Y or X=Y=Z (where: X, Y, Z can be: C, N, O, S and X also can be replaced with: Cl, Br, I), being present for all five samples. It requires coupled analytical methods to give the correct conclusions for this spectral range;
- the 1660–1630 cm$^{-1}$ domain ($\nu_{C=O}$, from –CONH-) is specific to amide I and is found in samples: LSB1, LSB3 and CSB3. Amide I absorption band is due to the elongation vibrations of carbonyl groups. This domain is sensitive to conformation modifications due to addition of vegetable extracts in the fur. The asymmetric shape of this band is due to the varied content of fine structures that make up the fur structure. Another contribution to the band asymmetry is that of hydrogen bond vibrations;
- the 1530-1550 cm$^{-1}$ domain ($\delta_{NH}$, from –CONH-) is attributed to amide II. The band at 1550 cm$^{-1}$ shifts to smaller wavelength numbers, which indicates a strong denaturation for fur samples: LSB1, LSB3 and CSB3. For the other two samples, amide II is situated beneath the detection limit of the device. Amide II absorption band is given by N-H deformation and C-N elongation modes. Bands at 1660 and 1550 cm$^{-1}$ provide information regarding the relative degree of degradation, through their position and absorbance. If shifts of these bands and absorbance modifications are found, it is obvious that structural changes have taken place;
- the denaturation degree determined by the amide I/ amide II, transmittance ratio has values over 1.0 for sample LSB1, proving the start of this process, supported also by the difference between the two frequencies ($\Delta\nu$), which has a value higher than 100. Amide I/ amide II ratio is large because OH groups contribute, absorbing in the same spectral domain;
- oxidation with $\nu$C=O group formation was emphasized for fur samples CSB1 and CSB3, the process being triggered and sustained by various substances in the environment;
- in the 680– 450 cm$^{-1}$ domain a few low intensity absorption bands are present, attributed to deformation variations of CH, OH, NH groups and these are present for all 5 fur samples with and without immobilized vegetable extracts.

In conclusion, fur samples CSB1 and CSB3 interact with the environment (air) by unsealing quicker than the others due to the oxidation phenomenon. The presence of thyme extract favours this phenomenon. Fur samples LSB1 and LSB3 undergo structural changes with the addition of vegetable composition, which encourages a slower release of bioactive principles into the atmosphere. The presence of lavender acts as fixative not allowing release of volatile materials in the air so quickly as in the case of the other samples.

*UV-VIS spectral analysis*

From the spectral analysis of aqueous extracts obtained by immersing samples in time, a shift of peaks characteristic to bioactive principles from immobilized extracts to higher wavelengths is noticed, which indicates a change of the interaction of the sample with the solvent.

UV-VIS fingerprint spectrum for lavender in ethylic alcohol presents absorption peaks at: 207 nm, 306 nm, 473 nm, 666 nm. UV-VIS fingerprint spectrum of thyme in ethylic alcohol presents absorption peaks at: 247 nm, 316 nm, 666 nm. Sage in ethylic alcohol has peaks in UV-VIS fingerprint spectrum at 300 nm and 260 nm wavelengths.

The purpose of this study was to obtain a release rate (as a measure of release time) of bioactive principles of: lavender, thyme, sage and of their concentration in saline aqueous solution (simulation in vitro) depending on the immersion time. Furs treated with vegetable extracts have

behaviour similar to sponges releasing bioactive principles in the environment or in salt water; there is a continuous interaction phenomenon. Experimental results for samples treated by immersion in vegetal extract blends are presented in in figure 1-8, in comparison with samples treated by spraying:

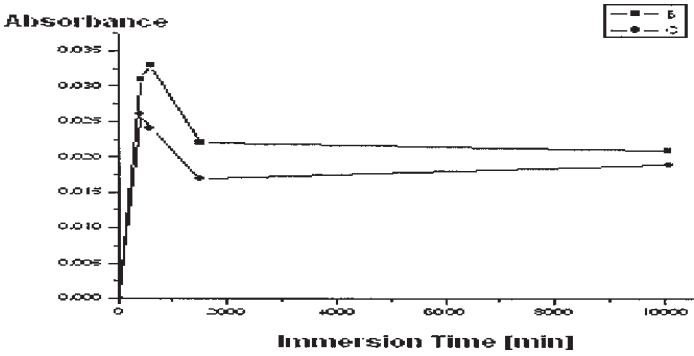


Fig.1. Dependency of lavender bioactive principles absorbance released in the salt water in time for samples LSB3 - ■ and LSB1- • (at λ= 207 nm)

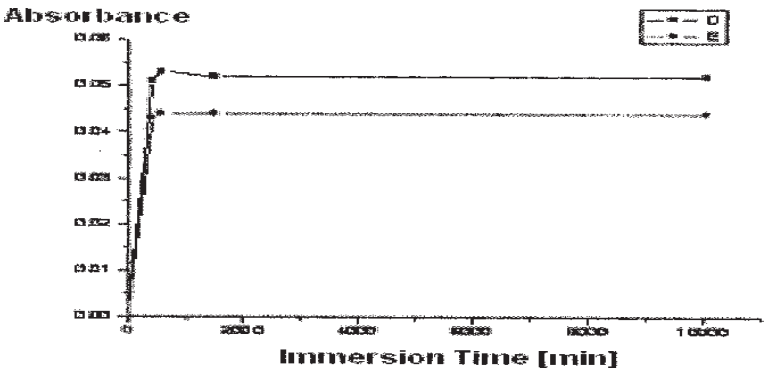


Fig.2. Dependency of sage bioactive principles absorbance released in the salt water in time for fur samples LSB3 - ■ and LSB1- • (at λ= 260 nm)

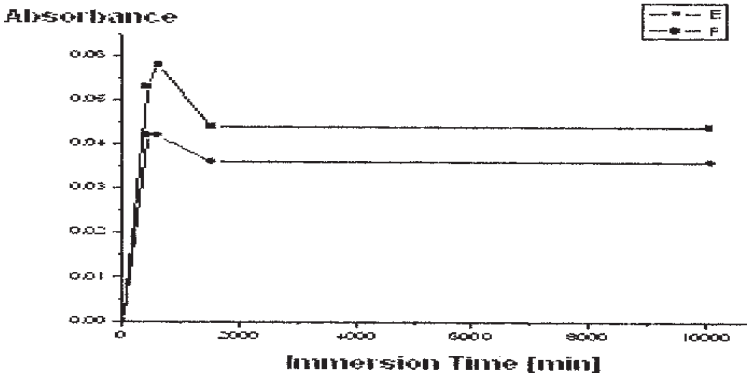


Fig.3. Dependency of thyme of bioactive principles absorbance released in the salt water in time for fur samples CSB3- ■ and for CSB1- •(at λ= 247 nm)

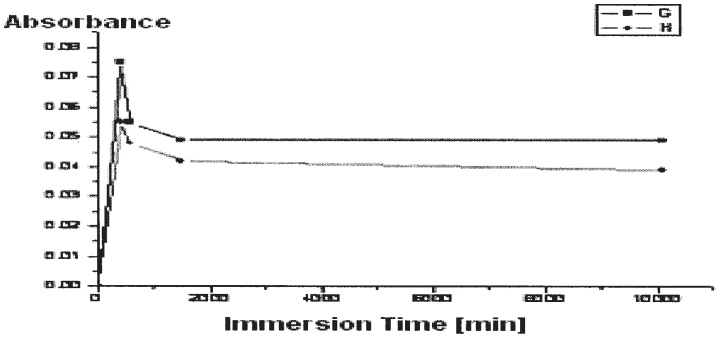


Fig.4. Dependency of sage bioactive principles absorbance released in the salt water in time for fur samples CSB3- ■ and for CSB1- • (at λ= 260 nm)

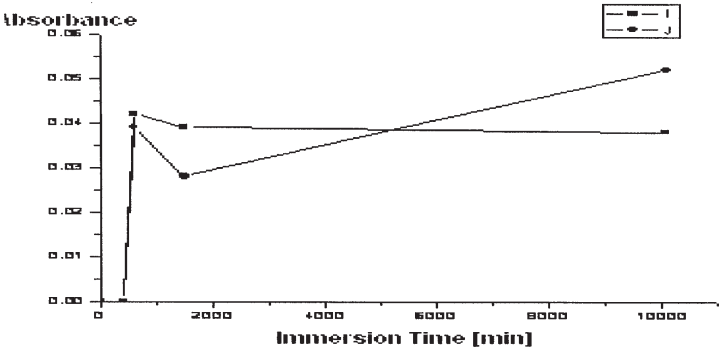


Fig.5. Dependency of lavender bioactive principles absorbance released in the salt water in time for fur samples LSB4 - ■ and LSB2 - • (at λ= 207 nm)

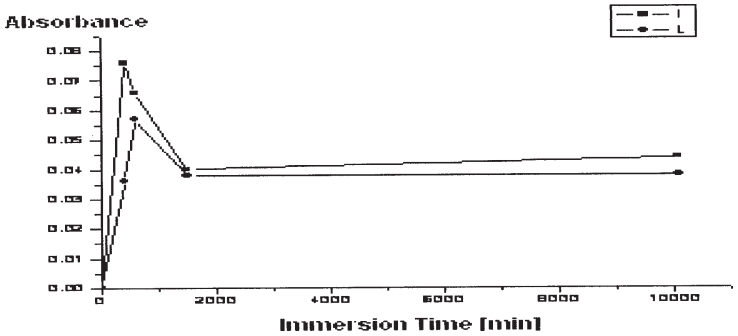


Fig.6. Dependency of sage bioactive principles absorbance released in the salt water in time for fur samples LSB4 - ■ and LSB2 - ● (at λ= 260 nm)

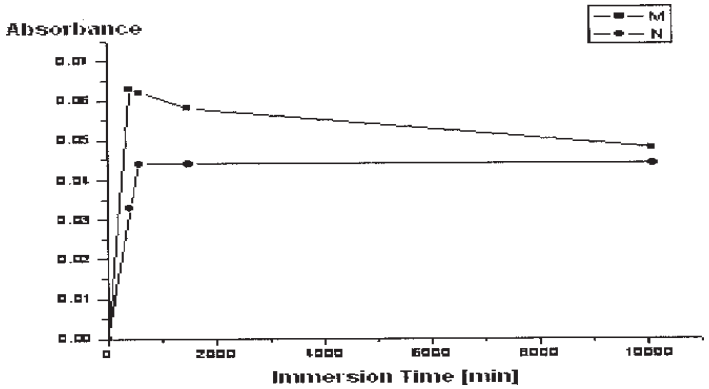


Fig.7. Dependency of thyme bioactive principles absorbance released in the salt water in time for fur samples CSB4 - ■ and CSB2- ● (at λ= 247 nm)

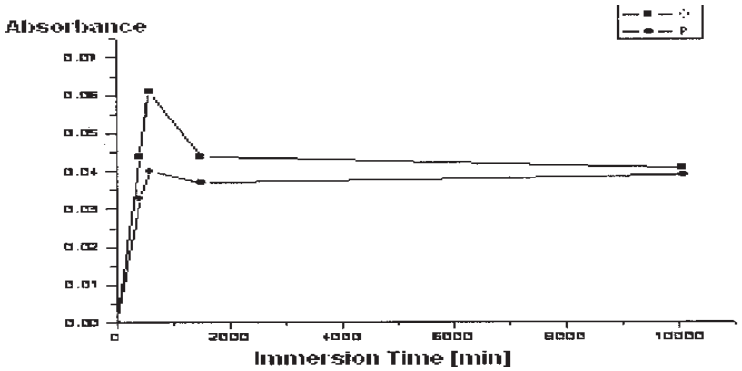


Fig.8. Dependency of sage bioactive principles absorbance released in the salt water in time for fur samples CSB4 - ■ and CSB2- ● (at λ= 260 nm)

It is noticed that in the case of fur samples treated by immersion in volatile oils blends the release of bioactive principles in salt water is much more emphasized than those treated by spraying, due to higher concentration corresponding to higher values of absorbances. In samples LSB2, CSB2, LSB4 and CSB4 it is noticed that the bioactive principles release is continuous over a 9 day interval, encouraged by the fact that they have been left in contact with air (fig.1-8). Modeling the release speed of bioactive principles from studied furs can be done based on the following types of releasing profiles:

-release of zero order, where the release speed is constant;

-release of order one, where the release speed is proportional to the weight of active agent released from the system until time t;

-release proportional to square root of time.

Theoretic results have led to the conclusion that the appropriate model in this case is the release of order 1. Release of order 1 profile has been chosen because there are 2 values of absorbance (initial and final), and release rates are very low. A new software was elaborated that can calculate the release rate of bioactive principles of the 8 analysed fur samples. The software is created in VBA [9] with the interface of Excel Worksheet. Dependency of the release speed of active principles depending to fur treatement (by immersion or by spraying), storage type (sealed or free) and plant extract combinations are presented in figure 9-11 :

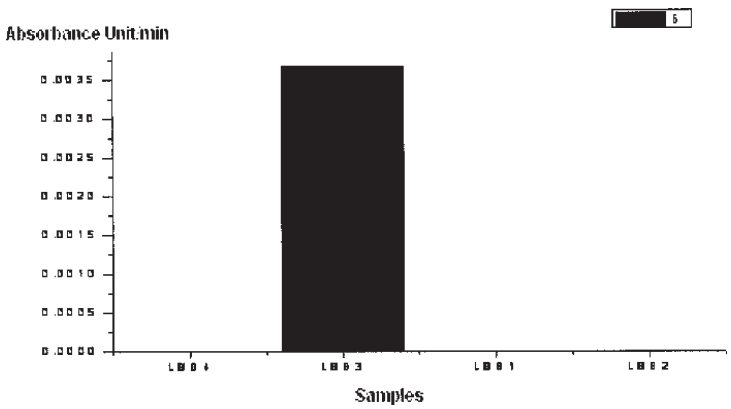


Fig.9. Release rate of lavender bioactive principles from sealed stored fur samples (LSB1 and LSB3) compared to the free stored ones (LSB2 and LSB4)

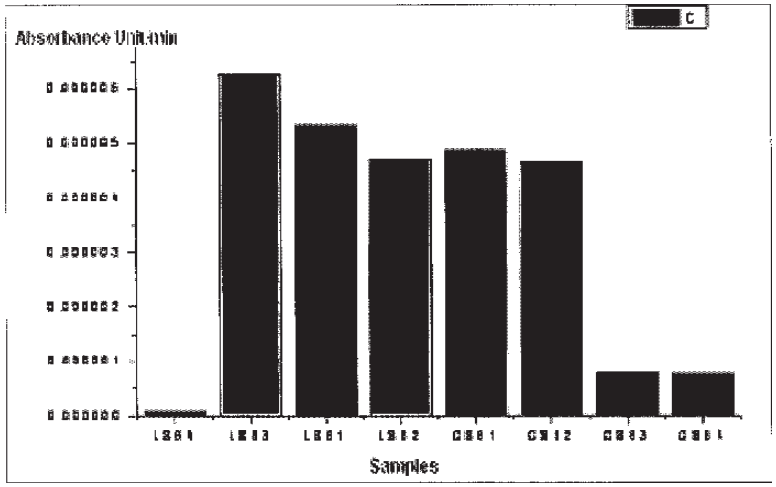


Fig.10. Release speed of sage bioactive principles in different blend combinations, from sealed stored fur samples (LSB3, LSB3, CSB3, CSB4,LSB4) in comparison with free stored fur samples (LSB1, LSB2, CSB1, CSB2)

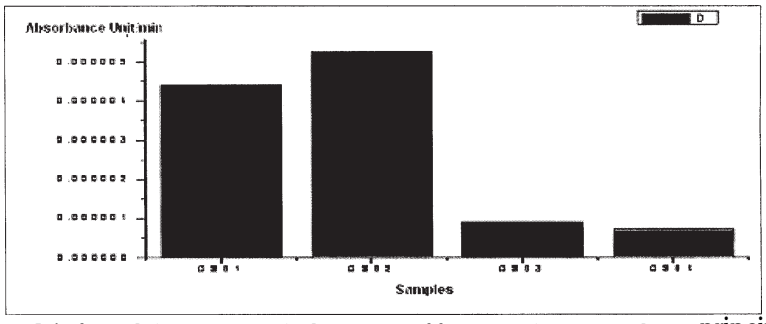


Fig.11. Release speed of thyme bioactive principles from sealed stored fur sample (CSB1 and CSB3) in comparison with free stored fur samples (CSB2 and CSB4)

It is found that non-sealed storage of fur samples treated by immersion or spray coating makes release of plant extracts in aqueous environment to be done with a higher rate (except for sage in LSB combination). Lavender and thyme extracts are better preserved in the wool structure, in the conditions of storing fur samples in sealed foils, and the combination of sage and thyme (in sealed storage conditions) favours the preservation of sage bioactive principles. It is noticed that the lowest release rate of active principles is that of lavender, regardless of the treatment type. For treatment of furs by immersion, it is found that the release rate of active principles is much smaller than for spray coating.

## Conclusions

Embedding the bioactive extracts within the medical furs provides a progressive release of the active principles because of the retard effect of hydrophilic collagenous and keratin microstructures.

Conducted research has led, also, to the following results:

-selecting plant extracts and remanent combinations on medical fur support: lavender, sage and thyme;

-establishing the storage type for medical furs treated by immersion or by spray coating, sealing in foils or keeping as such. It was established that by storing medical furs in sealed foils, the release rate in aqueous environment is smaller compared to non-sealed storage;

-by FT/IR-ATR spectrometry an oxidative interaction was determined in the case of the sample treated with thyme extract stored by sealing (CSB1) and an interaction with lavender in the case of sealed sample (LSB1);

-release rate of bioactive components of vegetable extracts from treated fur samples have been determined by means of an original software by simulating release in time in saline solutions and analysis of concentrations by UV-VIS spectroscopy;

-for most samples, bioactive principle release in saline water takes place gradually for approximatively 420 min and then it reaches a constant concentration;

-it was established that in the case of non-sealed storage of fur samples treated by spray coating, the release of active principles in aqueous environment is done with a higher rate (except for sage in LSB combination). Lavender and thyme extracts are preserved the longest in the wool structure, in conditions of storing the fur samples in sealed foils, and the sage and thyme blends (in sealed storage conditions) favours preservation of sage bioactive principles;

-models of fur items for medical use have been created which can be treated with plant extracts and used for medical or everyday use.

The use of plant extracts blends, wellknown for the bioactive principles content based on polyphenols ($\lambda$=666 nm), flavones ($\lambda$=473 nm), hydrolysable tannins etc. represents a valuable route for ecological medical furskins manufacture with new prophylactic, anti-inflamatory, bactericidal or relaxing properties.

The subject had been also approached by other researchers [10].

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