

## Characterization of Surface Treatments of Cork Stoppers by FTIR-ATR

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A general method is described for the identification of paraffin- and silicone-based surface treatments applied to single-piece natural and 1 + 1 (cork agglomerate with two natural cork disks) cork stoppers used to seal wine bottles. The method is based on Fourier transformed infrared spectroscopy (FTIR) and attenuated total reflectance (ATR) analysis of ready-for-use stoppers. The absorbance in seven wavelength bands selected as the most characteristic (2916 and 2850  $\text{cm}^{-1}$ , for paraffins, and 2963, 1258, 1079, 1010, and 787  $\text{cm}^{-1}$ , for silicones) was measured for both kinds of stoppers. Univariate analysis of the results enabled identification of stoppers that had received surface treatment by measuring the absorbance in two of the selected bands, representing paraffins and silicones, respectively. The type of surface treatment used was identified by discriminant analysis. Using this technique, we constructed a mathematical model using the seven bands studied. The model correctly classified 100% of the stoppers used to construct it and 91.7% of the stoppers used for validation.

**KEYWORDS:** Cork stopper; surface treatment; paraffin; silicone; quality control; FTIR-ATR

### INTRODUCTION

Cork stoppers are important for the preservation of wine and, consequently, its quality (1, 2). To improve sealant properties and wine preservation, the stopper surface is treated with paraffins and silicones. This operation, also known as softening, is part of the stopper finishing process, which also includes the previous operations of washing and application of a colored coating. By the application of a thin layer of paraffin and silicone ( $\approx 50 \mu\text{m}$  thick) (3), the cork surface can be smoothed out, producing a continuous seal between the cork and the glass. This treatment also facilitates insertion into and extraction from the bottle of the stopper, by reducing friction. In addition, stopper impermeability is improved. Thus, these treatments lubricate cork stoppers, facilitating the operation of bottling machines, improving extraction, preventing wine leaks, and acting as a barrier against absorption and migration (4–6).

Among the cork stoppers available on the market, the ones used most often to seal wine bottles are the natural (traditional single-piece cork stopper) and 1 + 1 (technical) types. The 1 + 1 stoppers have a cork agglomerate body to which two natural cork disks, about 5 mm thick, are attached at each end. There are some differences in the performance of these two types of stoppers, both from a physical and mechanical perspective and with respect to cork–wine interactions. These are due to differences in composition as well as in the orientation of the cork tissue on the surface of the stopper in contact with the

wine: in the natural stopper, the direction of fluid flow coincides with the longitudinal axis of cork tissue, being perpendicular to pores and parallel to growth layers. In contrast, in the disk of the 1 + 1 stopper, the direction of fluid flow is that of the radial axis of the tissue, parallel to pores, and perpendicular to growth layers (3).

Among the various factors that can influence wine preservation (dimensions of the bottleneck and stopper, type of wine, bottling conditions, and others) (7–9), the presence (and amount) of surface treatment of the stopper is very directly related to the mechanical properties of the seal and, therefore, to wine preservation, especially with regard to oxidation (10, 11).

To our knowledge, no method has been developed to date that enables identification of the coating applied to a given stopper. Likewise, we are not aware of any quality control procedures being used for these parameters by either the cork or the wine industry. However, the scientific literature contains many references, in regard to other materials, on methods for analyzing coating products and their raw materials (12–14): chemical, chromatographic, spectroscopic, and electrochemical methods; surface analysis methods such as ion and electron beam techniques, ultraviolet/visible spectroscopy, X-ray analysis, microscopy, and other spectroscopic techniques; particle size determination; thermal methods; and others.

Among the surface analysis techniques, FTIR spectroscopy with attenuated total reflectance (FTIR-ATR) has been widely used for the chemical and physical characterization of structures (15, 16). ATR is an IR sampling technique that measures the

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**Table 1.** Commercial Products for Surface Treatments Used in the Study

product	treatment
equalizer (colored coating dispersed in paraffin)	T2
reticulatable silicone with organic solvent	T3-A
reticulatable silicone without organic solvent	T3-B
aqueous emulsion of paraffin and silicone	T4-A
paraffin	T4-B1
silicone oil	T4-B2

**Table 2.** Identification of Analyzed Samples

	treatment	stopper type	sample code
T1	rinsed with water	1 + 1 natural	A-T1 N-T1
T2	T1 + washed with hydrogen peroxide + colored coating dispersed in paraffin	1 + 1 natural	A-T2 N-T2
T3-A	T2 + reticulatable silicone (with organic solvent)	1 + 1 natural	A-T3A N-T3A
T3-B	T2 + reticulatable silicone (without organic solvent)	1 + 1	A-T3B
T4-A	T2 + aqueous emulsion of paraffin and silicone	1 + 1 natural	A-T4A N-T4A
T4-B	T2 + paraffin + silicone oil	natural	N-T4B

changes in an infrared beam with totally internal reflection when it comes into contact with a sample. An infrared beam is aimed at a crystal with a high-refractive index at a certain angle. Internal reflectance results in an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. As this evanescent wave protrudes only 0.5–5  $\mu\text{m}$  beyond the crystal surface and into the sample, optical contact between the sample and the crystal must be optimized by applying pressure.

We used this technique in the present study because of its simplicity and speed, as well as the minimal preparation of the material required. The collected data were later analyzed using univariate and multivariate statistical techniques.

Therefore, the main objectives of our study were (i) to establish a fast and simple analytical method for determining if a given cork stopper has undergone surface treatment and the type of product used, (ii) to evaluate the potential of univariate (analysis of variance, ANOVA) and multivariate (canonical discriminant analysis and stepwise discriminant analysis) statistical methods for differentiating the various types of surface treatment of cork stoppers, and (iii) to produce a mathematical model to identify the type of treatment applied to a stopper.

## MATERIALS AND METHODS

**1. Reagents and Samples.** Single-piece natural cork stoppers ("extra" quality) and 1 + 1 cork stoppers subjected to different finishing processes were studied. **Table 1** lists the commercial chemical agents used in each operation, and **Table 2** describes the samples by type of finish and stopper.

As shown in **Table 2**, four main types of finish were studied: T1, water rinse; T2, water rinse followed by washing with hydrogen peroxide + equalizing (colored coating dispersed in paraffin); T3, treatment T2 followed by silicone treatment; and T4, treatment T2 followed by treatment with a mixture of silicone and paraffin. Silicone usually is dissolved in an organic solvent before application (T3-A), whereas the mixture of silicone and paraffin is applied generally as an aqueous emulsion (T4-A). In light of current trends to use manufacturing procedures which are more ecological and compliant with environmental regulations, we considered it interesting to investigate the influence of the use of different application methods. Consequently, 1 + 1 stoppers

**Table 3.** Assignments of Selected Bands from the Paraffin and Silicone FTIR-ATR Spectra

peak no.	frequency ( $\text{cm}^{-1}$ )	assignment
1	2963	C–H stretch $\text{CH}_3$ asymmetric
2	2916	C–H stretch $\text{CH}_2$ asymmetric
3	2850	C–H stretch $\text{CH}_2$ symmetric
4	1258	$\text{Si}(\text{CH}_3)_2\text{O}$ stretch symmetric
5	1079	Si–O–Si stretch symmetric
6	1010	Si–O stretch
7	787	Si–C bonding

to which silicone without organic solvent (T3-B) had been applied and natural stoppers treated successively with paraffin (T4-B1) and silicone lubricant (T4-B2) were also studied. Ten different samples were obtained, which were homogeneous in terms of surface treatment and type of stoppers.

Finishing processes were applied to cork stoppers at a pilot plant belonging to Catalonian Cork Institute, in Girona, Spain. This organization acquired stoppers and surface treatment products and applied the products to stoppers; they provided the finished stoppers and small samples of the treatment products used. We do not know the origin and exact composition of the treatment products, other than that they were commercial products that are widely used in the stopper industry, and that their composition basically included the products listed in **Table 1**.

**2. Infrared Spectroscopy.** The FTIR spectrometer was an FTIR460 Plus instrument from Jasco, equipped with a MIRacle ATR accessory from Pike Technologies, with ZnSe lenses and a single-reflection diamond ATR element. The crystal plate assembly of the MIRacle single-reflection ATR features a round plate design with a diameter of 1.8 mm in the centrally located sampling area. Resolution was  $4\text{ cm}^{-1}$ , and an average of 58 (autoaccumulation mode) spectra were accumulated to improve the signal-to-noise ratio. The contact pressure between clamp and sample was 10 psi. Data were collected using the Jasco Spectra Análisis program.

**3. Analytical Method.** A cork disk about 5 mm thick was obtained from each stopper by cutting one end with a blade. For each sample, three disks were obtained from different stoppers and they were measured in duplicate (main data set). The proposed model was validated using two more disks obtained from each sample, which were analyzed once (validation data set). So, a total of eight determinations (spectra) were obtained for each sample. All FTIR-ATR spectra were recorded taking care that the point of contact of the lens did not coincide in any case with pores present on the surface of the material. Baseline correction was applied to all spectra, adjusting the line at 900, 1800, and  $3000\text{ cm}^{-1}$ . The noise level was set to 0.02 in absorbance.

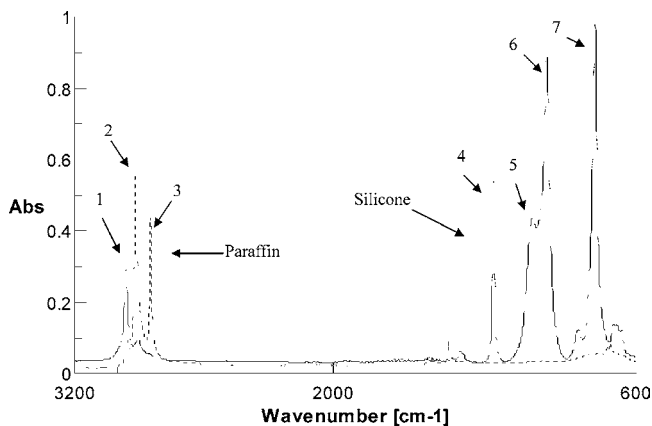
The chemical agents used in the surface treatments were also analyzed by FTIR. They were deposited directly on the ATR accessory once the solvent had evaporated, after 24 h at room temperature.

In the FTIR-ATR spectra obtained, the absorbance at the frequency of each of the bands selected was measured (see **Table 3**).

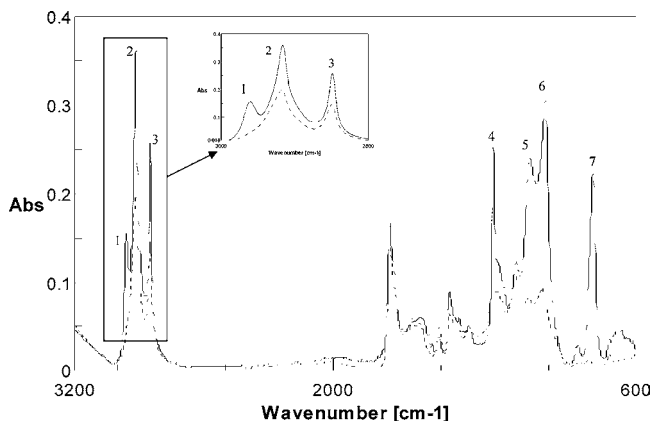
**4. Statistical Analysis.** Differences between treatments were evaluated, and the most characteristic variables (IR spectra frequencies) or combinations of variables were identified using several statistical analyses: univariate (ANOVA) and multivariate analyses (stepwise discriminant analysis, canonical discriminant analysis). All analyses were made with BMDP7M and CANDIS programs from BMDP Release 7 (BMDP Statistical Software, 1992) and SAS (Statistical Analysis System, Version 8), respectively. In stepwise discriminant analysis, all frequencies were forced to enter the model to ensure a better result.

## RESULTS AND DISCUSSION

**Analysis of Surface Treatment Products.** The FTIR-ATR spectra obtained from the T3-B (reticulatable silicone) and T4-B1 (paraffin, see **Table 1**) are shown in **Figure 1**. These spectra allowed us to select characteristic bands (listed in **Table**



**Figure 1.** FTIR-ATR spectra of reticulatable silicone (—) without organic solvent (product T3-B) and paraffin (···) after eliminating organic solvent (product T4-B1).



**Figure 2.** FTIR-ATR spectra of a 1 + 1 stopper without treatment, T1 (···) and of a 1 + 1 stopper treated with an aqueous emulsion of paraffin and silicone, T4-A (—).

3) for paraffin and silicone, which were components of the products used for surface treatments. Bands 1258, 1079, 1010, and 787  $\text{cm}^{-1}$  are specific of silicone. Bands 2963, 2916, and 2850  $\text{cm}^{-1}$ , which are less specific, corresponding to C–H bonds, had intensities that differed greatly in both types of compounds. The 2963  $\text{cm}^{-1}$  band is due to  $\text{CH}_3$  and occurs in silicones exclusively as the only alkane. It also occurs as a minor feature in paraffins as a terminal  $\text{CH}_3$  group. The 2916 and 2850  $\text{cm}^{-1}$  bands are due solely to the  $\text{CH}_2$  functional groups, which do not occur in silicones but are dominant in paraffins and present in the cork material. Therefore, there may be some overlap between  $\text{CH}_2$  from paraffins and from underlying cork (Figures 1 and 2).

**Analysis of Cork Stoppers.** The type spectra of a nontreated 1 + 1 stopper (T1) and of a 1 + 1 stopper treated with an aqueous emulsion of paraffin and silicone (T4-A), in which the selected bands (Table 3) are clearly identifiable, are shown in Figure 2. These spectra exhibit bands corresponding to the cork matrix, the most intense occurring at 1735  $\text{cm}^{-1}$ , due to carbonyl bonds, mainly from suberin, and bands at 1010–1300  $\text{cm}^{-1}$ , due mainly to carbohydrate and lignin C–O. The latter can overlap with those of silicone.

Although the effective cork coating thickness is theoretically greater than the depth of penetration of the beam, underlying cork spectra is detected, probably due to a very thin, irregular, or fractured treatment layer. Some operations with spectra (such as subtraction of spectra from nontreated stoppers) failed to yield clear results, probably because of the heterogeneity of underlying

cork material. Multivariate statistical analyses may help to solve this problem because they can use a large range of variables (absorbances at different wavelengths) and combinations thereof to differentiate nontreated stoppers (T1) from the rest. When these methods are used, small differences in several wavelengths may help to classify observations that are not clearly different.

**Table 4** lists, for the selected bands, mean absorbance values and the associated standard deviations for the six measurements made of each sample (main data set). All silicone-related bands showed absorbance values below the noise level (0.02) in samples T1 and T2, which were not treated with silicone.

**Statistical Analysis.** In all the bands considered, univariate analysis of the variance (ANOVA) disclosed significant differences ( $p < 0.0001$ ) between samples. In the bands related to the presence of silicone, it is evident that this was due mainly to the presence or absence of silicone. In the case of the other two bands (2916 and 2850  $\text{cm}^{-1}$ ), the differences are attributable mainly to the lower absorbance of T1 samples, which is appreciable in both bands, of the natural stopper and 1 + 1 stopper samples. This is because the amount of paraffin added by T2 treatment, although small, is enough to produce a significant increase in absorbance.

The Coefficient of Determination between these two bands is very high ( $R^2 = 0.999$ ). Examination of individual data (not shown) confirmed that the absorbance of T1 stoppers was in every case lower than 0.260 in the 2916  $\text{cm}^{-1}$  band and lower than 0.185 in the 2850  $\text{cm}^{-1}$  band. In contrast, in T2 stoppers, the minimum absorbances were 0.295 and 0.215, respectively, with the exception of a single observation that displayed values of 0.246 and 0.176. Consequently, measurement of the absorbance at any of these bands and establishment of a cutoff value for each (for example, 0.277 for 2916  $\text{cm}^{-1}$  or 0.200 for 2850  $\text{cm}^{-1}$ ) allowed the correct classification of 23 of the 24 observations of T1 and T2 samples (96%).

On the other hand, although the differences between samples in some bands can be significant, univariate analysis does not allow to readily differentiate between observations on stoppers that have received treatments T3 and T4. Multivariate analysis was used to overcome this problem, being more efficient than univariate analysis because in the latter variables are analyzed independently.

Multivariate analysis was carried out in two steps: first, discriminant analyses (canonical and stepwise) were conducted for all samples of the main data set; analyses were then repeated only for samples that were not clearly differentiated in the first step. All analyses yielded significant results ( $p < 0.001$ ) for all the statistics considered (Wilk's Lambda, Pillai's Trace, Hotelling-Lawley Trace, and Roy's Greatest Root).

The results of analysis were interpreted using, in addition to group means and the matrix of coefficients (not included), the canonical structure (correlation between canonical and original variables) shown in Table 5. The total cumulative proportion reached with the first canonical function (Can1) was 0.8468, which increases to 0.9428 if the second (Can2) is added and reaches 0.9819 if the third canonical function (Can3) is also included. The squared canonical correlations obtained were 0.99 and 0.93 for the first and second canonical functions (Can1 and Can2), respectively.

The data are plotted in Figure 3, grouped by finishing process applied (Table 2), as projections on the first two axes. The results obtained after canonical analysis of the data (Table 5) indicate that the first canonical axis correlated closely with the presence of silicone bands and clearly separated T1 and T2

**Table 4.** Means and Standard Deviations ( $n = 6$ ) of Absorbances at the Characteristic Bands by Stopper Types and Surface Treatments

stopper type	treatment code	2963 $\text{cm}^{-1}$	2916 $\text{cm}^{-1}$	2850 $\text{cm}^{-1}$	1258 $\text{cm}^{-1}$	1079 $\text{cm}^{-1}$	1010 $\text{cm}^{-1}$	787 $\text{cm}^{-1}$
1 + 1	T1		0.190 $\pm$ 0.225	0.136 $\pm$ 0.026				
	T2		0.362 $\pm$ 0.030	0.263 $\pm$ 0.023				
	T3-A	0.111 $\pm$ 0.005	0.336 $\pm$ 0.032	0.242 $\pm$ 0.022	0.162 $\pm$ 0.015	0.163 $\pm$ 0.015	0.178 $\pm$ 0.019	0.085 $\pm$ 0.016
	T3-B	0.149 $\pm$ 0.010	0.354 $\pm$ 0.028	0.254 $\pm$ 0.021	0.227 $\pm$ 0.022	0.227 $\pm$ 0.023	0.273 $\pm$ 0.031	0.174 $\pm$ 0.024
natural	T4-A	0.162 $\pm$ 0.006	0.352 $\pm$ 0.026	0.249 $\pm$ 0.020	0.271 $\pm$ 0.014	0.248 $\pm$ 0.011	0.333 $\pm$ 0.028	0.241 $\pm$ 0.028
	T1		0.211 $\pm$ 0.028	0.149 $\pm$ 0.021				
	T2		0.345 $\pm$ 0.061	0.250 $\pm$ 0.045				
	T3-A	0.096 $\pm$ 0.019	0.286 $\pm$ 0.049	0.206 $\pm$ 0.035	0.144 $\pm$ 0.032	0.145 $\pm$ 0.033	0.161 $\pm$ 0.041	0.070 $\pm$ 0.028
	T4-A	0.126 $\pm$ 0.011	0.255 $\pm$ 0.049	0.180 $\pm$ 0.036	0.215 $\pm$ 0.025	0.198 $\pm$ 0.022	0.249 $\pm$ 0.036	0.161 $\pm$ 0.039
	T4-B	0.133 $\pm$ 0.006	0.474 $\pm$ 0.033	0.350 $\pm$ 0.027	0.196 $\pm$ 0.021	0.182 $\pm$ 0.018	0.223 $\pm$ 0.033	0.142 $\pm$ 0.041

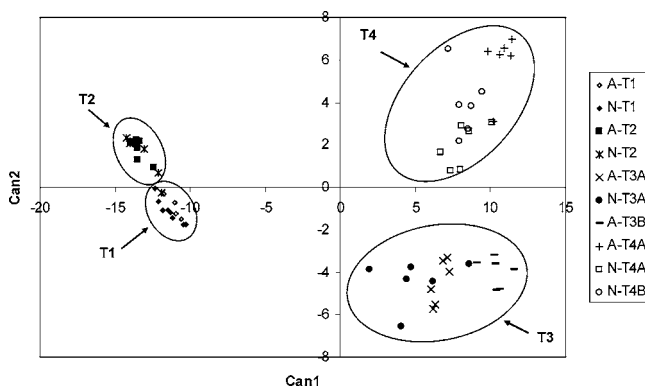
**Table 5.** Correlations between Canonical and Original Variables (Total Canonical Structure) Obtained in the Analysis of Data from All Samples

frequency ( $\text{cm}^{-1}$ )	Can 1	Can 2	Can 3
2963	0.988788	0.095957	0.040962
2916	0.364106	0.341772	0.812855
2850	0.345317	0.335286	0.831082
1258	0.974687	0.151781	-0.035702
1079	0.980758	0.089278	-0.014013
1010	0.959691	0.175456	-0.044962
787	0.888080	0.320281	-0.074609

samples from T3 (A, B) and T4 (A, B) samples, as is logical in light of the results of univariate analysis.

The second canonical axis correlates with the bands characteristic of paraffins and also clearly separates T1 from T2 samples and T3 from T4 samples. Only one observation of the T2 group, the exception detected by univariate analysis, is included in the T1 group. This indicates that multivariate analysis did not improve the results of univariate analysis insofar as differentiating T1- from T2-treated stoppers. On the other hand, the analysis did not allow differentiation between the types of stopper used (natural and 1 + 1) or between the various application methods.

In an attempt to improve the separation between treatments, multivariate analyses were repeated using only observations on T3-A-, T3-B-, T4-A-, and T4-B-treated stoppers. In this case, the cumulative proportion of total dispersion was 0.5182 with the first variable (Can1), 0.9001 with the second (Can2), and 1.0000 with the third (Can3). The coefficients of each variable with the canonical variables obtained are provided in **Table 6**. This model allowed for correct classification of 100% of the observations on stoppers of the calibration set. The classification

**Figure 3.** Canonical discriminant analysis of data from all samples. Plot of Can2 vs Can1.**Table 6.** Coefficients of Canonical Variables Obtained in the Stepwise Analysis of Samples T3 and T4

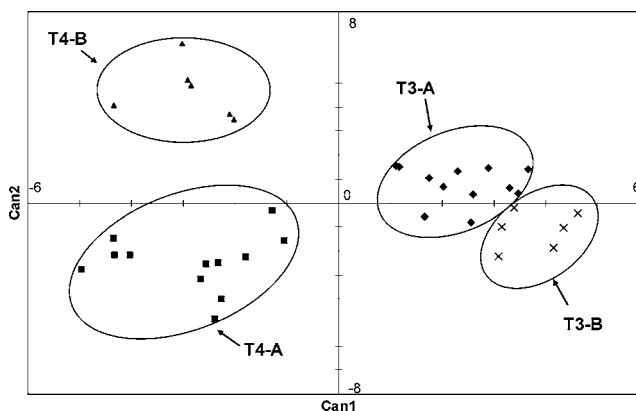
frequency ( $\text{cm}^{-1}$ )	Can 1	Can 2	Can 3
2963	100.12946	-145.15605	-114.82286
2916	6.46430	-59.88147	211.74842
2850	-27.34450	130.37238	-274.68315
1258	-311.90335	-68.64839	65.46975
1079	348.63784	48.89615	-102.96270
1010	-69.10664	11.76743	57.62066
787	24.77833	38.33499	-28.09413

matrix was identical to the one obtained by the jackknifed classification method, which is a special case of the general cross-validation method. The good results obtained with the latter classification confirm the stability of the model.

As can be observed in **Figure 4**, the analysis performed notably improved the separation between groups. The first axis enables separation of T3 and T4 treatments. To appreciate the effect of the application method, it is necessary to use the axis Can2, which separates T4-A from T4-B, and T3-A from T3-B.

Stepwise discriminant analysis provides classification functions that allow us to assign new observations to one group or another based on measurements of the original variables (absorbance at each frequency). **Table 7** describes the classification functions, which allow new cases to be assigned to the group for which this function yields the highest value.

The model was validated using data obtained from the validation collection. The percentage of correctly classified observations in this case was 91.7% (11 of 12). The only incorrectly classified case was possibly due to the heterogeneity of cork, a natural product, and to the presence in the cell wall of compounds that are chemically similar to those applied

**Figure 4.** Stepwise discriminant analysis of data from samples T3 and T4. Plot of Can2 vs Can1.

**Table 7.** Constants and Coefficients of Classification Functions Obtained in the Stepwise Analysis of Samples T3 and T4

variable	T3-A	T3-B	T4-A	T4-B
2963	1464.5468	628.796	1562.918	2294.228
2916	-1175.960	-1921.955	-1285.460	-1821.010
2850	1362.194	2635.996	1431.422	2073.285
1258	-364.296	855.766	1396.348	-914.114
1079	791.301	-614.465	-1048.116	1565.899
1010	45.214	324.123	292.478	-283.281
787	-642.816	-559.219	-860.353	-577.940
constant	-59.211	-73.295	-81.119	-98.054

(paraffins), such as natural cork waxes. Thus, to improve the model, it would be desirable to increase the number of observations from the main set.

Finally, it must be noted that no significant differences were found between groups based on the type of stopper (natural and 1 + 1) used. We thus concluded that tissue orientation had no significant effect on absorbance in the studied bands, and that the classification procedure described can be used indistinctly with both types of stopper.

**Conclusions.** The proposed analytical method enables identification of the presence of surface treatments in cork stoppers. By determination of the absorbance at the selected bands, it was possible to differentiate the type of treatment applied to a given stopper as well as the application method used. However, FTIR-ATR analysis did not enable determination of the type of stopper (1 + 1 or natural).

This method correctly classified 91.7% of a set of stoppers not used to construct the model, on which a single measurement was made. We conclude that the characteristics of the proposed method make it certainly applicable in industry settings.

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