**DOI:** 10.29298/rmcf.v13i72.1186

Article

# Identificación preliminar de maderas de pinos mexicanos mediante espectroscopía ATR-FTIR

# Preliminary identification of woods from Mexican pines by ATR-FTIR spectroscopy

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Fecha de recepción/Reception date: 12 de julio de 2021
Fecha de aceptación/Acceptance date: 2 de junio del 2022

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**Abstract**

A wide variety of species of the genus *Pinus* are widely distributed in Mexico, and are of great commercial importance, so proper identification of its wood is important. This is not an easy task, due to the anatomical and chemical characteristics of the pines; for this reason, the potential of an ATR-FTIR spectral reference library of wood (spectral library) was investigated. The spectra of woods have enough differences to implement an identification process by spectral comparison. Spectral library was created using samples from xylotheque in the Department of Wood, Cellulose and Paper (*Universidad de Guadalajara*), which have been rigorously identified. The spectra of nine pine species (*Pinus arizonica*, *P. ayacahuite*, *P. devoniana*, *P. douglasiana*, *P. durangensis*, *P. oocarpa*, *P. patula*, *P. pringlei*, and *P. pseudostrobus*), were obtained from three different places, so that spectral library has 27 spectra. To determine the viability of method, other samples from xylotheque were analyzed, different from those of spectral library, of five species (*P. ayacahuite*, *P. devoniana*, *P. oocarpa*, *P. pseudostrobus*, and *Cupressus arizonica*), obtaining in three cases the highest correlations for correct species, and a second place for the other two. The use of a spectral library is a quick method, which can help in identification of wood and establish its origin. The technique could be improved by developing a spectral and statistical treatment that considers the particularities of lignocellulosic materials.

**Key words:** ATR-FTIR Spectroscopy, spectral library, wood, wood chemistry, Mexican pines, xylotheque.

**Resumen**

Una gran variedad de especies del género *Pinus* están ampliamente distribuidas en México, y son de importancia comercial, por lo que la identificación apropiada de su madera es relevante. Esta no es una labor sencilla, debido a las características anatómicas y químicas de los pinos; por ese motivo, se investigó el potencial que tiene para dicha tarea una base de datos computarizada de espectros ATR-FTIR de madera (espectroteca). Los espectros de las maderas poseen suficientes diferencias para implementar un proceso de identificación por comparación espectral. La espectroteca se creó con tablillas de la xiloteca del Departamento de Madera, Celulosa y Papel (Universidad de Guadalajara), que se han identificado de manera rigurosa. Se obtuvieron los espectros de nueve especies (*Pinus arizonica*, *P. ayacahuite*, *P. devoniana*, *P. douglasiana*, *P. durangensis*, *P. oocarpa*, *P. patula*, *P. pringlei* y *P. pseudostrobus*) de tres lugares distintos, para un total de 27 espectros. Para determinar la viabilidad del método, se analizaron otras tablillas de la xiloteca, correspondientes a cinco taxones

(*P. ayacahuite*, *P. devoniana*, *P. oocarpa*, *P. pseudostrobus* y *Cupressus arizonica*); del análisis resultaron las correlaciones más altas para las especies correctas en tres casos, y un segundo lugar para las otras dos. El uso de una espectroteca es un método rápido que ayuda en la identificación de una madera, así como para establecer su origen. La técnica podría mejorarse mediante el desarrollo de un tratamiento espectral y estadístico que considere las particularidades de los materiales lignocelulósicos.

**Palabras clave:** Espectroscopía ATR-FTIR, espectroteca, madera, química de la madera, pinos mexicanos, xiloteca.

# Introduction

Wood is one of the most important forest resources with great versatility, which explains why since immemorial time, all cultures have given it different uses. The number of timber species is huge, with very particular characteristics, whose composition can even vary from one region to another. These features include physical resistance, color, smell and density, to name a few; diversity makes wood a highly valuable material, and certain species, as favorites for very specific applications (Grebner *et al*., 2014).

Consequently, accurate identification of wood is an important activity, which demands specialized knowledge. This process usually starts with the provenance and characteristics of the tree, when possible; without antecedents, it becomes more difficult. Wood identification work covers anatomical aspects, both macroscopic and microscopic, and even for an expert sometimes, it means a hard job (Gasson, 2011). Chemical information can complement conventional anatomical characterizations to provide better results in the identification of timber species (Singh, 2016).

Wood has an extremely complex chemical environment that is not yet fully understood. It is made up of macromolecules (cellulose, hemicelluloses, lignin) that serve as structural material, and extractive compounds. The former are closely related to each other, which means that they cannot be separated without significantly modifying their structure (Rowell *et al.*, 2013).

Therefore, it is convenient to carry out a chemical analysis directly on the wood, without making any changes in it. Spectroscopic techniques are suitable for this purpose and FTIR in the attenuated total reflectance modality (ATR-FTIR) in particular, allows direct analysis of the sample surface, down to around 5 μm deep (Ochiai, 2015). The molecular vibrations that are recorded in the spectra are representative of the functional groups, and are subject to the chemical environment in which they are present (Tasumi, 2015). The use of ATR-FTIR for wood identification has been studied, but with modification of the samples, which means that valuable information is obviously lost (Traoré *et al*., 2018; Sharma *et al*., 2020).

The objective of this research study was to identify mexican pine wood by obtaining ATR-FTIR spectra of unmodified samples. In this way, the analysis is fast, non-destructive, and if a portable spectrophotometer is available, the determinations can be made *in situ*. The key is the creation of a computerized database of ATR-FTIR spectra of pine wood (spectrotheque), to make the identification through spectral comparison. The aim is to determine the viability of the method for the task of identifying mexican pine woods, as well as to visualize the adjustments that can be made to improve the results, and later extend the technique to other types of wood.

It was established that the study was made with pines, for two reasons: the first, because pines comprise approximately 70 % of the timber forest production in Mexico (Inegi, 2021); the second, being conifers evolutionarily prior to broadleaves, they have a less complex anatomical structure and chemical composition, thus, they have fewer characteristics that differentiate them from each other (Keeley, 2012). The last aspect means that identifying pine trees can be a difficult task, even for experts, making it the ideal field to test wood identification tools.

## Materials and methods

15.0 × 6.8 × 1.0 cm wood tablets from the xylotheque of the Department of Wood, Cellulose and Paper of the *Universidad de Guadalajara* were used. The collection brings together more than 700 samples, from a wide variety of genera and species, whose identification was carried out by several researchers from the Department and the Institute of Botany of the University itself. In 1985, Dr. Ezequiel Montes Ruelas started the wood collection, later researchers such as Dr. José Antonio Silva Guzmán have worked on it; the material was collated and certified by Prof. Hans Georg Richter of the Johann Heinrich von Thünen-Institut at the University of Hamburg. The xylotheque is registered with code in the International Association of Wood Anatomists (IAWA).

The spectrotheque for this research was built with nine *Pinus* wood species, from different regions of Mexico; of each species, three tangentially cut sapwood tablets were considered, for which there was a total of 27 samples. A smooth surface is required for spectroscopic analysis, which was achieved by using a DWP362 DeWalt sander. Table 1 shows the species studied and the origin of the woods with which the spectrotheque was made.

**Table 1.** Species and origin of the *Pinus* samples with which the spectrotheque was made.

| Species | Region | Variety |
|---|---|---|
| *P. arizonica* Engelm. | *Chihuahua* | var. *stormiae* Martínez |
| | *Durango* | |
| | *Nuevo León* | |
| *P. ayacahuite* Ehrenb. ex Schltdl. | *Durango* | var. *veitchii* (Roezl) Shaw |
| | *Puebla* | var. *brachyptera* Shaw |
| | *Estado de México** | var. *veitchii* (Roezl) Shaw |
| *P. devoniana* Lindl. | *Jalisco, Tapalpa* | var. *cornuta* Martínez |
| | *Jalisco, Zapopan* | |
| | *Michoacán* | |
| *P. douglasiana* Martínez | *Jalisco* | |
| | *Michoacán* | |
| | *Estado de México** | |
| *P. durangensis* Martínez | *Chihuahua* | f. *quinquefoliata* Martínez |
| | *Chihuahua* | |
| | *Durango* | |
| *P. oocarpa* Schiede | *Chiapas* | var. *ochoterenae* Martínez |
| | *Jalisco, Tapalpa* | |
| | *Michoacán* | |
| *P. patula* Schiede ex Schltdl. & Cham. | *Oaxaca (plantación)* | var. *longipedunculata* Loock ex Martínez |
| | *Puebla* | |
| | *Veracruz* | |
| *P. pringlei* Shaw | *Guerrero* | |

| Species | Region | Variety |
|---|---|---|
| | *Michoacán* | |
| | *Estado de México** | |
| | *Guerrero* | var. *oaxacana* (Mirov) S.G. Harrison |
| *P. pseudostrobus* Lindl. | *Jalisco* | |
| | *Michoacán* | |

* The sample was collected in the country, but the data of the state of origin are not recorded.

Before the analyses, the samples were stored for five days in the Biomaterials Laboratory at 35 % relative humidity -permanently- and 25 °C, which are the optimal conditions for working with the analytical equipment. Three ATR-FTIR spectra of the spring sapwood section were obtained from each of the 27 tablets, at different points on the surface, to verify that they were the same and to ensure that the selected spectrum was representative of the wood.

A Perkin-Elmer Spectrum GX spectrophotometer was used, with a MIRacle PIKE brand accesory for attenuated total reflectance (ATR), simple reflection and diamond crystal. The spectra obtained comprise the mid-infrared region (4 000 to 700 $cm^{-1}$) with a spectral resolution of 4.00 $cm^{-1}$ and 16 scans; diamond absorbs between 2 300 and 1 800 $cm^{-1}$, so in principle readings in this range should be ignored (there are no bands in this area corresponding to wood). To ensure adequate contact between the sample and the ATR crystal, the accesory press was always kept fixed to exert the maximum pressure, 50 $kg \cdot cm^{-2}$.

Using the 10.4 version Spectrum software (PerkinElmer, 2013), the spectra were changed to absorbance, corrected baseline, smoothed using the Savistky-Golay algorithm with 9 points, and normalized (Savistky y Golay, 1964).

With the 4.3.8.210 version AssureID Method Explorer software (PerkinElmer, 2014) the model by class analogy (SIMCA, Soft Independent Modeling of Class Analogy) was generated, which is based on the analysis of principal components (PCA, Principal Components Analysis). In this way, the variations that occur in the data set of all pine wood spectra are analyzed, and it helps to recognize patterns. The SIMCA algorithm produces a hypersphere that encapsulates the 99 % confidence surrounding a population, so the probability of a sample being misclassified is 1 %.

In order to have an additional confirmation that the spectra of the pine woods have enough differences to not consider them the same, the COMPARE process of the Spectrum software (PerkinElmer, 2013) was used. In this, the COMPARE® algorithm, patented by Perkin-Elmer, is used to calculate the correlation between pairs of absorbance spectra. In determining the value of the correlation, filters are applied in order to weight the effect of aspects such as resolution, intensity and noise of the signal; the software criterion to define if two spectra are equal to each other is that they have a correlation greater than 0.9800 with the use of the algorithm.

The spectral database (spectrotheque) was built with the spectra of the woods, with the Spectragryph software version 1.2.15 (Menges, 2020), which allows the management and analysis of spectrophotometer files of various brands. In the software, the search for spectral similarity is based on the calculation of the Pearson correlation coefficient of the entire spectrum, the indicated interval or specific spectral characteristics. This database also included species information and the geographical origin of the wood.

The searches in the spectrotheque were made based on four criteria: the complete spectrum (CP, 4 000 to 700 $cm^{-1}$), complete without considering the absorption region of the diamond (CP-SD, 4 000 to 700 $cm^{-1}$ in which the 2 750 to 1 780 $cm^{-1}$ interval is omitted), the fingerprint region (DC, 1 780 to 700 $cm^{-1}$) and the position of the highest peak in this fingerprint region (DC-PA, 1 780 to 700 $cm^{-1}$).

In order to verify that the searches in the spectra library threw satisfactory results, tests were carried out with the ATR-FTIR spectra that make it up, so the 27 samples were analyzed one by one. All were correctly identified under the four search criteria.

To establish the performance of the search in the database to identify wood, tablets from the xylotheque were used. Four pine woods of the same species that make up the spectrotheque were chosen, from different collection places: *Pinus ayacahuite* Ehrenb. ex Schltdl. (*Oaxaca*, from a plantation), *P. oocarpa* Schiede (*Chiapas*), *P. pseudostrobus* Lindl. (Mexico City) and *P. devoniana* Lindl. (*Michoacán*). By way of comparison, the spectrotheque was also tested with *Cupressus arizonica* Greene (*Coahuila*), which, although it is not a pine, it is a conifer of the Pinales order.

# Results and Discussion

The 27 ATR-FTIR spectra of pine wood that comprise the spectra library are shown in Figure 1. All the spectra are very similar, as expected since they are woods of the same genus; the bands observed correspond essentially to the carbohydrate fractions (cellulose, hemicelluloses) and lignin, which are the structural components of wood.

The most characteristic bands are those of OH groups (3 335 $cm^{-1}$), C-H bonds (2 935 $cm^{-1}$), C=O in carbohydrates and lignin (1 705 $cm^{-1}$), C=C of conjugated ring in aromatic alcohol (1 645 $cm^{-1}$), lignin aryl ring stretching (1 510 $cm^{-1}$), C-H symmetric bending (1 420 $cm^{-1}$), C=O ring stretching in aryl ring of lignin (1 265 $cm^{-1}$) and C-O stretching in carbohydrate ring (1 025 $cm^{-1}$) (Özgenç *et al.*, 2017; Sekhar *et al.*, 2017).

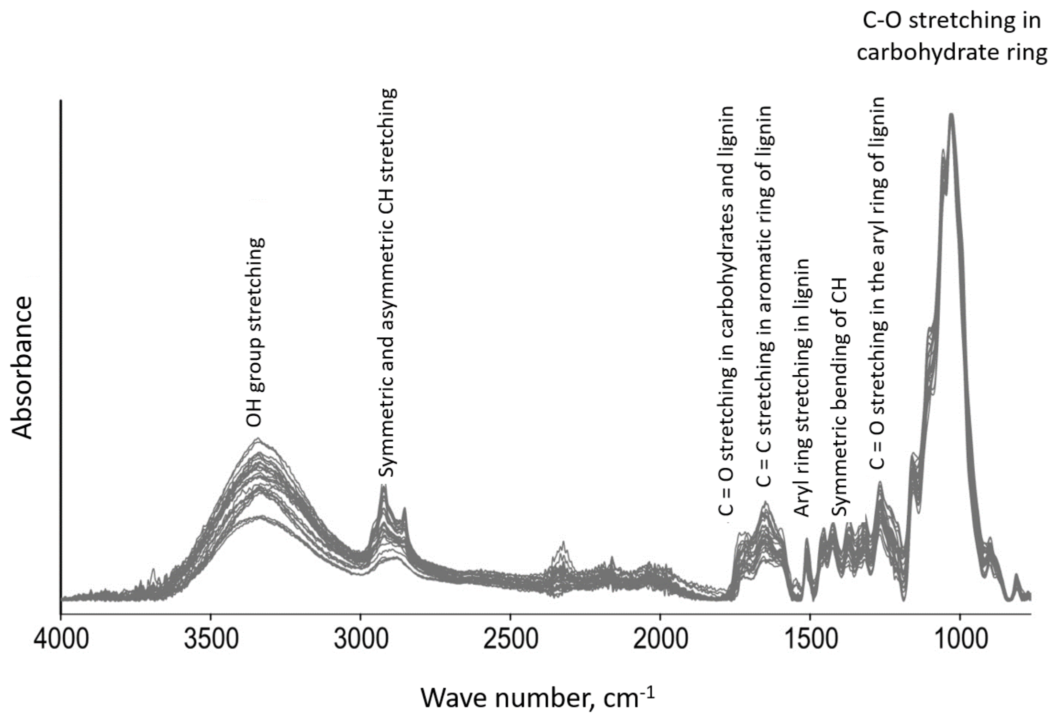


**Figure 1.** ATR-FTIR spectra of the 27 *Pinus* tablets that comprise the spectrotheque, with the assignment of the main bands.

There are some minor differences in the intensities of the bands, and in the peaks of the finger region, 1 750-1 550 $cm^{-1}$; these small differences can be enough to differentiate the woods, although not with the naked eye, so the use of specialized tools is necessary.

Calibration was made for all species, from which coefficients of determination between 0.98 and 0.99 were obtained when taking into account the 3 301 points that each spectrum comprises. For illustrative purposes, Figure 2 shows the spectra of *Pinus oocarpa* from *Michoacán* and *Chiapas*, as well as the correlation between them.

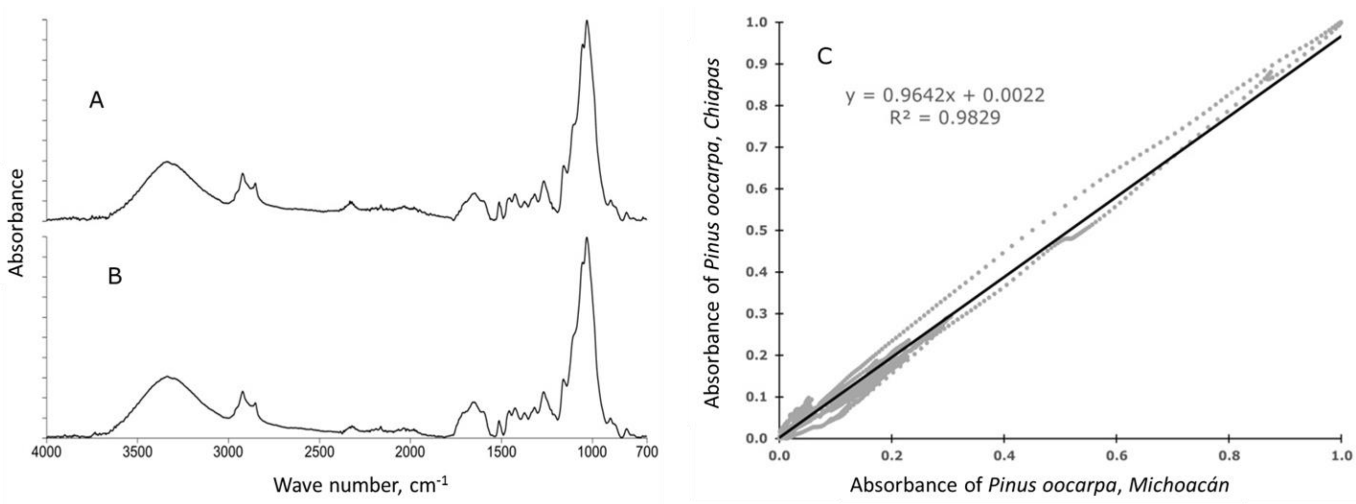


**Figure 2**. ATR-FTIR spectra of *Pinus oocarpa* Schiede woods from *Michoacán* (A) and *Chiapas* (B); C) Comparison of the absorbances between the spectra.

Figure 3 shows the results of the comparison of *P. oocarpa* from *Michoacán* and *Jalisco*, in which a higher determination coefficient was calculated, which suggests that there are differences between the spectra that can help differentiate them geographically. It can also be seen that the bands do not present noise, so the smoothness of the tablets is correct for the analysis.

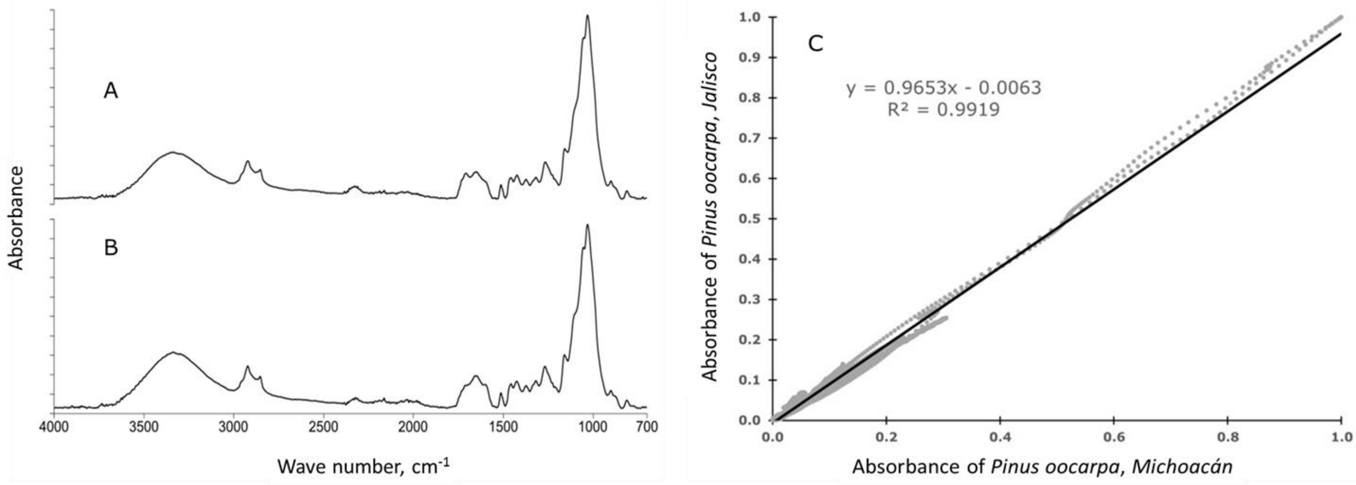


**Figure 3.** ATR-FTIR spectra of *Pinus oocarpa* Schiede woods from *Michoacán* (A) and *Jalisco* (B); C) Comparison of the absorbances between the spectra.

Furthermore, in the full wave number range (4 000-700 $cm^{-1}$), as well as the fingerprint region (1 780-700 $cm^{-1}$), and in all 27 spectra of the database, with the COMPARE option of the Spectrum software, correlations were less than 0.9800. Therefore, the spectra can be considered different from each other.

Regarding the SIMCA model, Figure 4 shows that there is only one group, which indicates that the spectra are highly similar, as a consequence of the fact that all the samples correspond to the genus *Pinus*; when soft and hard woods are analyzed, there are two clearly differentiated groups. In the group in Figure 4, a separation between the points (spectra) is noted, so despite their similarities, they present enough modalities to be able to differentiate them. This differentiation is multicausal, and has its origin in small variations in the chemical composition and the environmental conditions in which the trees grew.

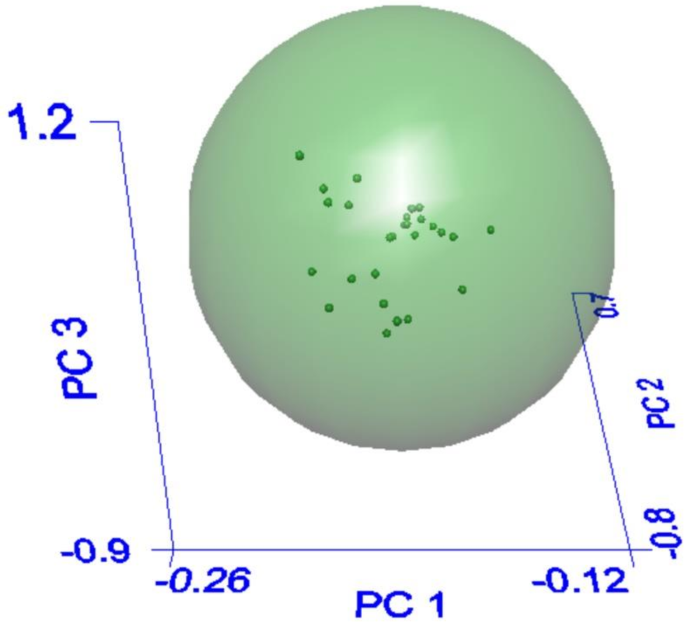


**Figure 4.** SIMCA model of the 27 pine woods that make up the spectrotheque.

In all database searches, the top ten highest correlations were listed in the software, and only the top three from each search are included in Tables 2 to 6.

**Table 2.** Spectrum library search results for *Pinus ayacahuite* Ehrenb. ex Schltdl. from *Oaxaca*.

| Complete spectrum, CP (4 000–700 $cm^{-1}$) | CP without crystal absorption region, CP-SD |
|---|---|

| No. | Corr | Species | Region | No. | Corr | Species | Region |
|---|---|---|---|---|---|---|---|
| 1 | 99.87 | *P. ayacahuite* Ehrenb. ex Schltdl. | *México** | 1 | 99.85 | *P. ayacahuite* Ehrenb. ex Schltdl. | *México** |
| 2 | 99.43 | *P. durangensis* Martínez | *Chihuahua* | 2 | 99.81 | *P. devoniana* Lindl. | *Michoacán* |
| 3 | 99.43 | *P. pringlei* Shaw | *Guerrero* | 3 | 99.64 | *P. pseudostrobus* Lindl. | *Guerrero* |
| **Fingerprint region, DC (1 780–700 $cm^{-1}$)** | | | | **DC highest peak position, DC-PA** | | | |
| **No.** | **Corr** | **Species** | **Region** | **No.** | **Corr** | **Species** | **Region** |
| 1 | 99.86 | *P. ayacahuite* Ehrenb. ex Schltdl. | *México** | 1 | 99.99 | *P. pseudostrobus* Lindl. | *Guerrero* |
| 2 | 99.56 | *P. durangensis* Martínez | *Chihuahua* | 2 | 99.98 | *P. ayacahuite* Ehrenb. ex Schltdl. | *Durango* |
| 3 | 99.55 | *P. pringlei* Shaw | *Guerrero* | 3 | 99.98 | *P. durangensis* Martínez | *Chihuahua* |

* The sample was collected in the country, but the data of the state of origin are not recorded. Corr = Pearson correlation.

**Table 3.** Spectrum library search results for *Pinus oocarpa* Schiede from Chiapas.

| **Complete spectrum, CP (4 000–700 $cm^{-1}$)** | | | | **CP without crystal absorption region, CP-SD** | | | |
|---|---|---|---|---|---|---|---|
| **No.** | **Corr** | **Species** | **Region** | **Núm.** | **Corr** | **Especie** | **Región** |
| 1 | 99.88 | *P. pringlei* Shaw | *Michoacán* | 1 | 99.83 | *P. pseudostrobus* Lindl. | *Michoacán* |
| 2 | 99.78 | *P. oocarpa* Schiede | *Chiapas* | 2 | 99.81 | *P. pringlei* Shaw | *Michoacán* |
| 3 | 99.53 | *P. patula* Schiede ex Schltdl. & Cham. | *Oaxaca* | 3 | 99.78 | *P. devoniana* Lindl. | *Michoacán* |
| **Fingerprint region, DC (1 780–700 $cm^{-1}$)** | | | | **DC highest peak position, DC-PA** | | | |
| **No.** | **Corr** | **Species** | **Region** | **No.** | **Corr** | **Species** | **Region** |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1 | 99.94 | *P. pringlei* Shaw | *Michoacán* | 1 | 99.99 | *P. pringlei* Shaw | *Michoacán* |
| 2 | 99.90 | *P. oocarpa* Schiede | *Chiapas* | 2 | 99.99 | *P. oocarpa* Schiede | *Chiapas* |
| 3 | 99.84 | *P. pseudostrobus* Lindl. | *Michoacán* | 3 | 99.99 | *P. arizonica* Engelm. | *Durango* |

Corr = Pearson correlation.

**Table 4.** Spectrum library search results for *Pinus pseudostrobus* Lindl. from Mexico City.

| **Complete spectrum, CP (4 000–700 cm$^{-1}$)** | | | | **CP without crystal absorption region, CP-SD** | | | |
|---|---|---|---|---|---|---|---|
| **No.** | **Corr** | **Species** | **Region** | **No.** | **Corr** | **Species** | **Region** |
| 1 | 99.60 | *P. pseudostrobus* Lindl. | *Jalisco* | 1 | 99.80 | *P. pseudostrobus* Lindl. | *Jalisco* |
| 2 | 99.49 | *P. pseudostrobus* Lindl. | *Guerrero* | 2 | 99.46 | *P. pseudostrobus* Lindl. | *Guerrero* |
| 3 | 99.45 | *P. ayacahuite* Ehrenb. ex Schltdl. | *Durango* | 3 | 99.37 | *P. patula* Schiede ex Schltdl. & Cham. | *Puebla* |
| **Fingerprint region, DC (1 780–700 cm$^{-1}$)** | | | | **DC highest peak position, DC-PA** | | | |
| **No.** | **Corr** | **Species** | **Region** | **No.** | **Corr** | **Species** | **Region** |
| 1 | 99.88 | *P. devoniana* Lindl. | *Jalisco* | 1 | 100.00 | *P. durangensis* Martínez | *Chihuahua* |
| 2 | 99.80 | *P. ayacahuite* Ehrenb. ex Schltdl. | *Durango* | 2 | 99.99 | *P. oocarpa* Schiede | *Jalisco* |
| 3 | 99.80 | *P. pseudostrobus* Lindl. | *Jalisco* | 3 | 99.99 | *P. oocarpa* Schiede | *Michoacán* |

Corr = Pearson correlation.

**Table 5.** Spectrum library search results for *Pinus devoniana* Lindl. from *Michoacán*.

| **Complete spectrum, CP (4 000–700 cm$^{-1}$)** | **CP without crystal absorption region, CP-SD** |
|---|---|

| No. | Corr | Species | Region | No. | Corr | Species | Region |
|---|---|---|---|---|---|---|---|
| 1 | 99.71 | *P. pringlei* Shaw | *Michoacán* | 1 | 99.71 | *P. devoniana* Lindl. | *Michoacán* |
| 2 | 99.55 | *P. devoniana* Lindl. | *Michoacán* | 2 | 99.68 | *P. pringlei* Shaw | *Michoacán* |
| 3 | 99.53 | *P. pseudostrobus* Lindl. | *Jalisco* | 3 | 99.67 | *P. durangensis* Martínez | *Chihuahua* |
| **Fingerprint region, DC (1 780–700 cm$^{-1}$)** | | | | **DC highest peak position, DC-PA** | | | |
| **No.** | **Corr** | **Species** | **Region** | **No.** | **Corr** | **Species** | **Region** |
| 1 | 99.81 | *P. pringlei* Shaw | *Michoacán* | 1 | 100.00 | *P. oocarpa* Schiede | *Jalisco* |
| 2 | 99.80 | *P. patula* Schiede ex Schltdl. & Cham. | *Oaxaca* | 2 | 99.99 | *P. durangensis* Martínez | *Chihuahua* |
| 3 | 99.78 | *P. durangensis* Martínez | *Chihuahua* | 3 | 99.99 | *P. oocarpa* Schiede | *Michoacán* |

Corr = Pearson correlation.

**Table 6.** Spectrum library search results for *Cupressus arizonica* Greene from Coahuila.

| **Complete spectrum, CP (4 000–700 cm$^{-1}$)** | | | | **CP without crystal absorption region, CP-SD** | | | |
|---|---|---|---|---|---|---|---|
| **No.** | **Corr** | **Species** | **Region** | **No.** | **Corr** | **Species** | **Region** |
| 1 | 99.80 | *P. arizonica* Engelm. | *Chihuahua* | 1 | 99.87 | *P. arizonica* Engelm. | *Chihuahua* |
| 2 | 99.64 | *P. arizonica* Engelm. | *Nuevo León* | 2 | 99.85 | *P. ayacahuite* Ehrenb. ex Schltdl. | *México** |
| 3 | 99.26 | *P. ayacahuite* Ehrenb. ex Schltdl. | *México** | 3 | 99.73 | *P. oocarpa* Schiede | *Michoacán* |
| **Fingerprint region, DC (1 780–700 cm$^{-1}$)** | | | | **DC highest peak position, DC-PA** | | | |
| **No.** | **Corr** | **Species** | **Region** | **No.** | **Corr** | **Species** | **Region** |
| 1 | 99.87 | *P. ayacahuite* Ehrenb. ex | *México** | 1 | 99.99 | *P. pringlei* Shaw | *México** |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | Schltdl. | | | | | |
| 2 | 99.82 | *P. arizonica* Engelm. | *Chihuahua* | 2 | 99.98 | *P. arizonica* Engelm. | *Nuevo León* |
| 3 | 99.78 | *P. pringlei* Shaw | *Guerrero* | 3 | 99.98 | *P. arizonica* Engelm. | *Chihuahua* |

* The sample was collected in the country, but the data of the state of origin are not recorded. Corr = Pearson correlation.

Table 2 shows the results for *Pinus ayacahuite* from *Oaxaca* in three of the four searches; the species had the best correlation with the sample from the same region, which is extensive to the country (Mexico* in Table 2). In the spectrum of the fingerprint region, considering the highest peak (DC-PA), *P. ayacahuite* was in second place, with a different region from the others.

Now, the spectrotheque includes samples of *P. ayacahuite* from three regions *(Durango*, *Puebla* and the country; the state of origin of the latter is unknown), while the analyzed sample originates from *Oaxaca*. It is interesting to note here that in the searches in which *P. ayacahuite* is in the first place, it corresponds to the same sample, that of the country, which is a good indicator of the identification potential of the proposed methodology.

When the two full range spectra (CP and CP-SD) are considered, the first position has similar correlations, but the second and third positions correspond to different species. The only difference in these spectra is the noise in the absorption region of the diamond crystal; initially it was esteemed that the area should be discarded, which gave rise to the search criteria CP-SD. However, the CP spectrum was also used in the searches, for purely comparative purposes. It is noteworthy that the full spectrum gives the same result as the fingerprint region, a point that should be reviewed in detail in the other runs.

Another point to highlight from the results is that in all cases the correlations were greater than 99 %. Spectragryph (Menges, 2020) used Pearson's correlation, which is not the same as that used in Spectrum software (Perkin-Elmer, 2013), and generally gives very high values, which can be a problem. For example, the fourth and fifth positions in the CP-SD spectrum are *P. arizonica* Engelm. (*Chihuahua*) and *P. pseudostrobus* (*Michoacán*), which have practically the same correlation as third place.

The Spectragryph software (Menges, 2020) uses more decimal places in the Pearson correlation, but by displaying only two, the selection criteria is not clear, and can create confusion. The effect is even more marked in the search with the position of the highest peak in the fingerprint region (DC-PA): the difference between first and tenth place is only 0.04 %, and in the interval appear the three samples of *P. ayacahuite* from the spectrotheque in positions 2, 5 and 7, with minimal differences in their correlations.

In regard to *Pinus oocarpa*, in the four searches it is not in the first place (Table 3), but in three of them it is the second, with the same origin. This last aspect is important, which, added to being in the first three positions, is a good result. In the case of the CP-SD search, *P. oocarpa* is not in the first three places, it appears up to the seventh position with a 99.59 % correlation, a difference of 0.24 % with the first place. Consequently, the other three criteria are better options.

Again the full spectrum (CP) gives similar results to those of the fingerprint region, but now they are not the same. With the two samples analyzed so far, the full spectrum has been giving better results than the CP-SD spectrum, which was not initially expected. In the region that was omitted (2 750 to 1 780 $cm^{-1}$) only some noise appears (Figure 1), and although the energy reaching the spectrophotometer detector drops drastically in that area, it does not occur abruptly and the reading of energy never reaches zero. It seems that the noise from the absorption zone of the diamond crystal contains characteristics that are recognized by the software in the comparison process, and that can help the identification.

In the DC-PA search, to state that *P. oocarpa* is in second place is only considering the results of the software. The first three places have the same correlation value, and it is almost 100 %. Obviously, the search criteria is not right.

The analyzed *P. oocarpa* is from *Chiapas*, a tablet different from the one used for the construction of the spectrotheque. It can be seen in Table 3 that in the searches where *P. oocarpa* is in second place, the *Chiapas* region appears, which is correct; the other woods of *P. oocarpa* in the spectrotheque are from *Jalisco* and *Michoacán*, but it is the one from *Chiapas* that has the highest correlations. It is clear that regional characteristics of the studied species can be recognized in the ATR-FTIR spectra.

Table 4 shows the results for *Pinus pseudostrobus* native to Mexico City. When the complete spectra (CP and CP-SD) are considered, this species is in the first two positions, which also coincides in the regions. In the spectrotheque there are samples from *Guerrero*, *Jalisco* and *Michoacán*, and the fact that the searches have the same regions in the first places is striking.

With the DC-PA search, *P. pseudostrobus* does not appear in the first ten positions, but up to 12 with a correlation of 99.94 %, corresponding to the Guerrero region. Again, the type of search cannot be considered conclusive.

Regarding *P. devoniana* (Table 5), there are mixed results. With the use of the complete spectra, it appears in the second (CP) and first position (CP-SD), in both cases from the same region, *Michoacán*, which coincides with the origin of the sample.

With the DC and DC-PA spectra, there is a difference with respect to the previous cases: in the fingerprint region, the analyzed sample is not in the first three places, but up to the sixth position, and corresponds to the *Michoacán* region. In the DC-PA search it does not appear in the first ten positions, but up to 11$^{th}$ place, with a difference of 0.05 % from the first place.

Regarding *Cupressus arizonica* (Table 6) for the complete spectrum (CP), *Pinus arizonica* was obtained in the first two positions, and the highest correlation was obtained for the sample from *Chihuahua*. In the CP-SD search, first place was obtained, also for the *Chihuahua* sample.

In the fingerprint region it also appears in the first places, in second position in both cases (DC and DC-PA). There is a difference in the origin for the DC-PA search, in which *Nuevo León* appears first and then *Chihuahua*, but since they are the same regions, and since *Coahuila* is between the two states, it can be considered that there is consistency in the four searches with this feature.

Table 7 summarizes what was observed in the use of the spectrotheque to identify wood, showing the search definitions that gave the best results.

**Table 7.** Best search results for pine and cypress woods in the spectrotheque.

| **Species** | **Searches** | | | |
|---|---|---|---|---|
| | **CP** | **Region** | **DC** | **Region** |
| *Pinus ayacahuite* Ehrenb. ex Schltdl. *Oaxaca* | *P. ayacahuite* Ehrenb. ex Schltdl. | *México** | *P. ayacahuite* Ehrenb. ex Schltdl. | *México** |

| Species | Searches | | | |
|---|---|---|---|---|
| | *P. durangensis* Martínez | *Chihuahua* | *P. durangensis* Martínez | *Chihuahua* |
| | *P. pringlei* Shaw | *Guerrero* | *P. pringlei* Shaw | *Guerrero* |
| | **CP** | **Region** | **DC** | **Region** |
| *Pinus oocarpa* Schiede *Chiapas* | *P. pringlei* Shaw | *Michoacán* | *P. pringlei* Shaw | *México** |
| | *P. oocarpa* Schiede | *Chiapas* | *P. oocarpa* Schiede | *Chiapas* |
| | *P. patula* Schiede ex Schltdl. & Cham. | *Oaxaca* | *P. pseudostrobus* Lindl. | *Michoacán* |
| | **CP** | **Region** | **CP-SD** | **Region** |
| *Pinus pseudostrobus* Lindl. *Ciudad de México* | *P. pseudostrobus* Lindl. | *Jalisco* | *P. pseudostrobus* Lindl. | *Jalisco* |
| | *P. pseudostrobus* Lindl. | *Guerrero* | *P. pseudostrobus* Lindl. | *Guerrero* |
| | *P. ayacahuite* Ehrenb. ex Schltdl. | *Durango* | *P. patula* Schiede ex Schltdl. & Cham. | *Puebla* |
| | **CP** | **Region** | **CP-SD** | **Region** |
| *Pinus devoniana* Lindl. *Michoacán* | *P. pringlei* Shaw | *Michoacán* | *P. devoniana* Lindl. | *Michoacán* |
| | *P. devoniana* Lindl. | *Michoacán* | *P. pringlei* Shaw | *Michoacán* |
| | *P. pseudostrobus* Lindl. | *Jalisco* | *P. durangensis* Martínez | *Chihuahua* |
| | **CP** | **Region** | **CP-SD** | **Region** |
| *Cupressus arizonica* Greene *Coahuila* | *P. arizonica* Engelm. | *Chihuahua* | *P. arizonica* Engelm. | *Chihuahua* |
| | *P. arizonica* Engelm. | *Nuevo León* | *P. ayacahuite* Ehrenb. ex Schltdl. | *México** |
| | *P. ayacahuite* Ehrenb. ex Schltdl. | *México** | *P. oocarpa* Schiede | *Michoacán* |

* The sample was collected in the country, but the data of the state of origin are not recorded. Corr = Pearson correlation.

In all cases, and contrary to what was expected, the full spectrum (CP) gives the best results. Things are made easier, since the spectrum obtained in the equipment can be used directly, without eliminating specific spectral regions in the search. Only *P. devoniana* had a better result in the search without the crystal absorption zone (CP-SD), with an exchange between the first and second position.

Of five analyses, two with the full spectrum (CP) did not have the correct species in the first position, *Pinus oocarpa* and *P. devoniana*. But they were in second place, and in addition in all cases the results provided a good correspondence with the geographical area.

A good option in this technique is to consider the first positions as highly probable identifications. In fact, if the first two positions are taken in the full spectrum (CP) search, the correct species is between them; to have a slightly wider margin, it is proposed that the first three options be the ones considered to give a result.

The fingerprint region appears in Table 7 only in *Pinus ayacahuite* and *P. oocarpa*; obviously, when the full spectrum is not included, information is lost. It does not mean that this region does not have potential, it certainly has valuable information that can be used, but the spectra in the area must be treated in a different way. For example, to determine the area ratios in characteristic bands of lignocellulosic materials.

One aspect to highlight about this ATR-FTIR spectroscopy methodology is that the wood is used directly, without any modification; therefore, prior treatments are not necessary as those reported in the literature, which include grinding (Sharma *et al.,* 2020) or the use of specialized techniques such as the separation of anatomical and chemical components (Traoré *et al*., 2018). With the proposed methodology, the anatomical and supramolecular structure of the wood components is preserved, so valuable information that contributes to the identification process is not lost.

# Conclusions

With rigorously identified wood, a computerized ATR-FTIR spectra database, or spectrotheque, can be built to facilitate the work of sample identification. It is especially useful when the sawn wood has been lost, and part of the context that helps a correct identification has been lost, or when import or export procedures for commercial wood are carried out. ATR-FTIR analysis is fast, does not require modification of the wood and does not destroy the sample, so the characteristics of the original material are preserved.

The more spectra of woods that are available, even from the same species and from different regions, the better the results of the automated comparisons. Even if the wood under study is not in the records, the data sheds light on the species with the most similar spectra, and the information is helpful in the identification task.

The results give guidelines on the aspects of the technique that are susceptible to improvement, such as the development of a spectral treatment (increased resolution, area ratio of characteristic bands) and statistical treatment (specialized correlations) that considers the particularities of the materials lignocellulosic.

## Acknowledgements

The authors thank Dr. Raúl Rodríguez Anda and L. Q. Hilda Palacios Juárez, from the Wood Structure and Quality Laboratory of the Department of Wood, Pulp and Paper of the *Universidad de Guadalajara*, for their support in consulting the xylotheque.

## Conflict of interest

The authors declare no conflict of interest.

## Contribution by author

Héctor Jesús Contreras Quiñones: establishment of the work methodology, creation of the spectrotheque and writing of the document; David Alejandro Lizardo Aguayo: obtaining ATR-FTIR spectra, capturing in the spectrotheque and writing the document; Jesús Angel Andrade Ortega: review and correction of the manuscript; Carlos Alberto Ramírez Barragán: review and correction of the manuscript; Sara Gabriela Díaz Ramos: capture in the spectrotheque and writing of the document; Antonio Rodríguez Rivas: capture in the spectrotheque and writing of the document.

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