

# MOISTURE SORPTION PROPERTIES OF HARDWOODS AS AFFECTED BY THEIR EXTRANEOUS SUBSTANCES, WOOD DENSITY, AND INTERLOCKED GRAIN

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## ABSTRACT

Wood samples of nine tropical hardwoods from Peru and sugar maple from Quebec were selected for moisture sorption tests using a multiple step procedure at 25°C. Cold-water and hot-water extractives, sequential cyclohexane, acetone, and methanol extracts, ash content, wood density, and interlocked grain also were evaluated on matched samples. Wood extractives, interlocked grain, equilibrium moisture content (EMC), and hygroscopic stability were highly variable within and among wood species. Sequential extraction with organic solvents was the most suitable method for evaluating the effect of extractives on sorption behavior in tropical hardwoods. Cyclohexane extractives had a little influence on EMC. The acetone fraction was the most significant variable affecting EMC and hygroscopic stability of tropical hardwoods, while the methanol fraction had a negligible effect on the sorption behavior of these species. In general, EMC decreased and hygroscopic stability increased as the concentration of acetone extractives increased. The influence of these acetone-soluble compounds on EMC decreased as relative humidity increased. However, the acetone fraction of copaiba (*Copaifera* sp.), and probably caoba (*Swietenia* sp.), appeared to play a hydrophilic role in controlling the EMC of wood. Finally, EMC also decreased as wood density and interlocked grain increased.

*Keywords:* Ash content, density, equilibrium moisture content, extractives, interlocked grain, tropical woods.

## INTRODUCTION AND BACKGROUND

It is generally recognized that wood extractives affect the sorption properties of wood. Given their variable physical and chemical characteristics, these substances can exhibit hygroscopic, hydrophobic, or neutral behaviors. The sorptive response of wood extractives also can be affected by their location and distribution within wood, and by relative humidity (RH) and temperature conditions under which measurements are made. These different possibilities can explain some of the apparent discrepancies among literature reports, which concern the effect that these substances exert on the equilibrium moisture content (EMC) of wood.

Sorption isotherms of several species, including a number of tropical hardwoods, were reported by Higgins (1957) and Spalt (1958). Such early studies indicated that species containing high concentrations of extraneous substances show low EMCs, especially when relative humidity is above 50%. In his attempts to predict patterns of moisture release and gain in wood, Spalt (1958) applied the Hailwood-Horrobin theoretical model to sorption properties of sixteen temperate and tropical species. This model estimates the amount of moisture sorbed by wood in monolayers and in polylayers. Wood extractives had little effect on monolayer sorption, while they had an appreciable effect on polylayer sorption. Spalt's interpretation was only theoretical, since no determination of extractives was actually performed. Choong and

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Achmadi (1991) and Nzokou and Kamdem (2004) have since reported that extractives removal only affects the sorption behavior of wood at high relative humidities. Nearn (1955), on the other hand, found that the removal of extractives increases the EMC of wood, and that this increase is greater as RH increases. However, his study also should be considered as exploratory, since the sorption state was not controlled. Similar results have been obtained subsequently by Choong (1969) and by Taylor (1974).

The sorption behavior of wood, both before and after extraction, was studied by Wangaard and Granados (1967). Several woods were exhaustively extracted using a sequence of ethanol-benzene, ethanol, and hot water. Decreases in wood mass, which approached 17%, led to a noticeable increase in polylayer moisture sorption, as predicted by Spalt (1958), but the effect of the extraction treatment on wood structure, which lasted 10 to 20 days, was not even considered.

Other experiments have contradicted the results obtained from the aforementioned studies. Cooper (1974) indicated that wood extractives of black walnut (*Juglans nigra*) are more hygroscopic than its cell walls. Spalt (1979) has suggested that the extraction performed by Cooper (1974) was only partially effective in that small amounts of extractives were removed. This could have caused, in turn, only small effects on sorption compared to those attributed to the extraction treatment itself. However, Siberian larch showed similar trends to those reported for black walnut (Venäläinen et al. 2006).

Most of the studies previously mentioned were made using extracted samples. The extractions are usually conducted using various combinations of solvents, temperatures, and exposure times. Mantanis et al. (1994) have confirmed that solvents used for removing extractives are themselves disruptive to the cell walls. For example, substantial quantities of sugars can be removed, even with a mild procedure (80% ethanol for 2 hours). These sugars are derived primarily from hemicelluloses in the cell walls, which implies that the whole internal structure

of the cell walls was probably disrupted (Mantanis et al. 1994). In another approach, Jankowsky and Galvão (1979) evaluated hot-water extractable and ethanol-benzene extractable contents of wood material, which was matched to unextracted sorption samples. They confirmed what Nearn (1955) had found, that EMC decreases as concentrations of extractives increase and that this effect increases with RH. Unfortunately, only three woods were studied whereas the two types of extractions chosen gave quite similar results. Thus, little specific information exists regarding the different functions of wood extractives in controlling EMC. More detailed studies using a similar approach are required, but involving more species, while focusing on the location and distribution of these substances within wood. This would contribute to a better understanding of the effects of these substances on moisture sorption and other wood properties.

A number of tropical tree species exhibit interlocked grain patterns in their wood. For example, from 258 tropical hardwoods studied by Kribs (1950) about 75 percent were prone to interlocked grain. The influence of interlocked grain on wood mechanical properties has long been recognized (Hernández and Almeida 2003). Despite the increasing use of tropical hardwoods, few data are actually available regarding the effect of interlocked grain on the equilibrium moisture content of wood.

The objective of this study was to evaluate the effects of extraneous substances, wood density, and interlocked grain on the moisture sorption properties of nine tropical hardwoods and sugar maple wood. Sorption properties were evaluated with unextracted samples under five moisture conditions, which were obtained during the first full sorption cycle at 25°C. Matched material was used for interlocked grain measurements and chemical analyses. Several extraction procedures were used to ascertain the location and distribution of extractives within wood.

#### MATERIALS AND METHODS

Experiments were carried out with nine Peruvian tropical hardwoods: caoba or mahogany

(*Swietenia* sp.), cedro (*Cedrela* sp.), ishpingo negro (*Amburana cearensis* A.C. Smith), pumaquiro (*Aspidosperma macrocarpon* Mart.), copaiba (*Copaifera* sp.), palisangre negro (*Pterocarpus* sp.), estoraque (*Myroxylon* sp.), tahuarí (*Tabebuia serratifolia* Nichols), and palosangre (*Brosimum* sp.). These species are widely distributed throughout Amazonia. They were selected as representative tropical hardwoods, since they exhibit a wide range of densities, interlocked grain levels, types and amounts of extraneous substances, and different anatomical structures. The woods are widely used in furniture, flooring, decorative panels, and construction. Sugar maple (*Acer saccharum* Marsh.) was also included to represent a temperate hardwood having low amounts of extraneous substances.

Ten flatsawn boards were selected per species and stored at 20°C and 60% RH until EMC was reached. After conditioning, the boards were cut according to a pattern that yielded at least five parallel samples and three tangential samples (Fig. 1). These two types of matched samples were used to determine the EMC, parallel-to-grain and perpendicular-to-grain tangential compression strength, swelling, and oven-dry density. Results of the compressive and swelling properties are presented elsewhere. A sixth parallel sample was cut into two specimens for the interlocked grain evaluation. The tangential adjacent parts of the board were used to determine the concentrations of extraneous substances.

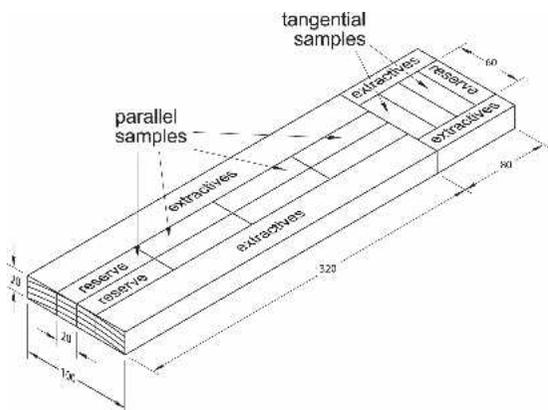


FIG. 1. Distribution of individual samples in the original board (dimensions in mm).

Five moisture sorption conditions were studied with the parallel samples. Three of them were repeated with the tangential samples. Longitudinal matching yielded eight comparable groups of 100 samples each, with each species represented by ten samples. The test material was all heartwood, except for sugar maple, which was sapwood. Contrary to the tropical hardwoods, the sapwood of maple is more important commercially than the heartwood.

Prior to the sorption experiments, all samples were oven-dried. This first drying, considered as the first desorption, was slow (377 hours) to reduce drying stresses in the material. The temperature was gradually increased to 100°C. After oven-drying, residual moisture and eventual internal drying tensions were reduced by holding the samples over phosphorus pentoxide at 25°C for 46 days. After this period of relaxation, all samples were weighed ( $\pm 0.001$  g) and their oven-dry dimensions were measured in all three principal directions with a micrometer ( $\pm 0.01$  mm). The oven-dry volume was calculated by multiplying the measurements of these three dimensions. Oven-dry density was calculated as the ratio of oven-dry mass to oven-dry volume.

Sorption tests were conducted simultaneously on all samples, using sorption vats described by Hernández and Pontin (2006). These vats provide temperature control of  $\pm 0.01^\circ\text{C}$  for extended periods, thus allowing control of RH in the various desiccators serving as small sorption chambers. For each sorption condition (100 samples), five desiccators (parallel samples) or four desiccators (tangential samples) were used, each containing twenty parallel samples or twenty to thirty tangential samples. All final sorption conditions were attained over saturated salt solutions or distilled water, with a multiple step procedure (Table 1), which lasted between 167 days (adsorption at 33% RH) and 450 days (adsorption at  $\approx 100\%$  RH). The number of steps, which ranged from 1 to 5, was chosen in order to achieve mild sorption with minimal or low internal tension. For each step of conditioning, control samples of each species were weighed periodically, without removing the wood from the desiccator. To avoid the effect of

TABLE 1. Sequence of moisture sorption conditions.

Experience	Group <sup>1</sup>	Chemical or saturated salt solution	Nominal relative humidity (%)	State of sorption	Length of each step (days)	Step <sup>2</sup>	
First adsorption	a33P	MgCl <sub>2</sub>	33	Adsorption	167	1*	
	a76P	NaBr	58	Adsorption	44	1	
	a76T				19		
	a76P	NaCl	76	Adsorption	175	2*	
	a76T				150		
	a100P	NaBr	58	Adsorption	39	1	
	a100T				22		
	a100P	KCl	86	Adsorption	27	2	
	a100T				21		
	a100P	H <sub>2</sub> O	100	Adsorption	384	3*	
	a100T				384		
	Second desorption	d58P	NaBr	58	Adsorption	41	1
		d58T				22	
		d58P	KCl	86	Adsorption	30	2
		d58T				27	
d58P		H <sub>2</sub> O	100	Adsorption	160	3	
d58T					148		
d58P		NaCl	76	Desorption	43	4	
d58T					36		
d58P		NaBr	58	Desorption	161	5*	
d58T					154		
d33P		NaBr	58	Adsorption	40	1	
d33P		KCl	86	Adsorption	28	2	
d33P		H <sub>2</sub> O	100	Adsorption	140	3	
d33P		NaCl	76	Desorption	44	4	
d33P		MgCl <sub>2</sub>	33	Desorption	133	5*	

<sup>1</sup> First letter: a = adsorption, d = desorption; number = RH in percent; last letter: P = parallel samples, T = tangential samples

<sup>2</sup> Asterisk shows the last step of sorption

hysteresis at saturation on the EMC (Hernández and Pontin 2006), desorption tests were made in the presence of bound water only. Therefore, final desorptions were preceded by an adsorption step over distilled water (Table 1).

As soon as each point of sorption was attained, the mass of the samples was measured to the nearest 0.001 g. This value, together with the oven-dry mass, were used to calculate the EMC, which was expressed as a percentage of oven-dry mass.

#### *Extraneous substances determination*

The tangential adjacent parts of the initial boards were ground to produce sawdust representing the original wood. The fragmentation procedure was intended to optimize the proportion of material retained between 20 and 70 mesh screens (0.210 to 0.841 mm), while mini-

mizing the production of very fine particles (Campbell and Bryant 1937).

#### *Cold-water solubility*

Cold-water solubility was determined according to ASTM D1110–84 (2001), with modifications to the filtration procedure used. Two air-dried samples of 2 g per board were mixed with 300 ml of distilled water. The slurries were agitated for 72 hours on a shaker set to 190 revolutions per minute. Material then was transferred to a tared filter paper, washed with cold distilled water, and oven-dried. Cold-water solubility (CW) is reported as the ratio of the oven-dry mass of extracted to unextracted oven-dry mass of wood (as a percentage).

#### *Hot-water solubility*

Two air-dried samples of 2 g per board were mixed with 250 ml of distilled water. Samples

were extracted in Erlenmeyer flasks provided with reflux condensers. After 3 hours of gentle boiling, material was transferred to a tared filter paper, washed with 1000 ml of hot distilled water, and oven-dried. Hot-water solubility (HW) is reported, on an oven-dry mass basis, as the ratio of extracted to unextracted wood (as a percentage).

#### *Sequential extraction with organic solvents*

Treatment of wood particles with a series of organic solvents of increasing polarity results in extraction that tends to be complete and selective. Sawdust was extracted sequentially in cyclohexane, acetone, and methanol. A similar protocol was suggested by Morgan and Orsler (1969) and applied successfully by Déon (1983). Cyclohexane was used instead of benzene as the former solvent poses less of a hazard to human health (Fengel and Przyklenk 1983). Two air-dried samples of 2 g per board were successively extracted in each solvent for 4 hours using soxhlets. Sawdust undergoing extraction was exposed to air for 14 hours between intermediate steps to allow the evaporation of the preceding solvent. Dry mass of each extract was obtained after vacuum evaporation and oven-drying. The solubility in each solvent was reported as the ratio between the oven-dry mass of the extracted fraction to unextracted oven-dry mass of wood (as a percentage).

#### *Ash content evaluation*

Ash content evaluation was determined according to ASTM D1102-84 (2001), except for the dimensions of particles. Two oven-dried samples (2.2 g per board) underwent high-temperature combustion (600°C for 4 hours). The ash content (ASH) is reported as the ratio of the oven-dry mass of the ash residue to oven-dry mass of wood (as a percentage).

#### *Evaluation of the interlocked grain*

The interlocked grain was determined by the splitting method (Hernández and Almeida

2003). Two air-dried samples of 20 mm (T) × 20 mm (R) × 35 mm (L) per board were split along a radial plane with a wedge-shaped knife mounted on a universal machine. Fibers in interlocked grain woods are inclined to the vertical axis of a tree at opposite angles, reaching approximately equal maxima first to one side (left spiral) and then to the other (right spiral). As a result, several interlocked patterns were produced in sample cross-sections. Micrographs of these sections were processed with image analysis techniques (Hernández and Almeida 2003). The maximum angular deviation (IG), in degrees, was estimated as the addition of the maximum left spiral angle to the maximum right spiral angle (in degrees).

#### *Exploratory analysis*

Multiple regression analyses were applied to the data sets to identify the principal variables affecting variation in EMC. Matrices of simple correlations were first calculated among the independent variables to identify sources of multicollinearity. This established which variables remained relatively independent when taken together for later analysis. As a result, a new wood density variable corrected for the extraneous substances ( $D_{oc}$ ) was used instead of the oven-dry wood density ( $D_o$ ), and was defined as follows:

$$D_{oc} = \frac{M_{oc}}{V_o} = \frac{M_o}{V_o} (1 - e) = D_o(1 - e) \quad (1)$$

where  $M_{oc}$  denotes the oven-dry mass without extraneous substances,  $V_o$  is the oven-dry volume,  $M_o$  is the overall oven-dry mass, and  $e$  is ash content plus extractives soluble in organic solvents (i.e., ASH + TOT). Correction of  $D_o$  was performed on the oven-dry mass only, but this does not take into account the effect that extraneous substances can have on the volume changes in wood.

Based on this exploratory study, five models of multiple regression were chosen to identify which extraneous substances best explained the moisture sorption behavior of the woods under

study. All models had three common independent variables: the corrected oven-dry density ( $D_{oc}$ ), ash content (ASH), and the interlocked grain (IG). The other independent variables were:

- Model 1: substances soluble in cold water (CW).
- Model 2: extractives soluble in cold water (CW), and substances soluble in hot water minus those soluble in cold water (HW-CW).
- Model 3: substances soluble in hot water (HW).
- Model 4: extractives soluble in a sequence of cyclohexane (CYC), acetone (ACE), and methanol (MET).
- Model 5: extractives soluble in organic solvents when taken together (TOT).

The stepwise regression method of REG procedure of SAS (2004) was used, with inclusion or exclusion of independent variables in the models set at the 0.10 probability level. The autonomy between independent variables was accomplished for the five models used. In most

cases, the coefficients of variation (CV) and the Mallows coefficients were minimal, as proposed by Draper and Smith (1981). Further tests of normality of variables and residual analysis were performed to verify the assumptions required for regression.

## RESULTS AND DISCUSSION

Extraneous substances and interlocked grain properties were quite variable within- and among species (Table 2). Cold-water extractives ranged from 1.6% in both sugar maple and cedro to 13.2% in copaiba. Concentrations of hot-water extractives were 1.3 to 2.5 times higher than those of cold-water extractives, and ranged from 2.8% in sugar maple to 17.9% in ishpingo negro (Table 2). Organic solvent-soluble extractives (TOT) were even higher and ranged from 2.2% (sugar maple) to 23.6% (ishpingo negro). The inorganic fraction (ASH) was a minor constituent in all wood samples, ranging from 0.01% in pumaquiro to 0.97% in copaiba. Interlocked grain was absent in sugar maple, but

TABLE 2. *Extractive substances, ash content, and interlocked grain of ten woods studied. Means and coefficients of variation (in italics).*

Wood species	Extractives		Successive extractions				Ash content ASH (%)	Interlocked grain IG (degree)
	Cold water CW (%)	Hot water HW (%)	Cyclohexane CYC (%)	Acetone ACE (%)	Methanol MET (%)	Total TOT (%)		
Caoba	4.65	8.49	1.65	3.11	4.66	9.42	0.87	2.8
	<i>16.9</i>	<i>4.9</i>	<i>10.8</i>	<i>23.4</i>	<i>9.9</i>	<i>4.3</i>	<i>17.2</i>	<i>70</i>
Cedro	1.58	3.41	1.20	0.73	1.29	3.22	0.93	3.3
	<i>21.6</i>	<i>26.0</i>	<i>26.6</i>	<i>35.0</i>	<i>30.4</i>	<i>29.1</i>	<i>10.1</i>	<i>72</i>
Ishpingo negro	7.04	17.91	3.82	14.74	5.08	23.64	0.88	12.5
	<i>6.1</i>	<i>12.0</i>	<i>7.0</i>	<i>13.6</i>	<i>17.3</i>	<i>11.6</i>	<i>14.9</i>	<i>27</i>
Pumaquiro	4.26	6.93	0.38	4.16	3.21	7.74	0.01	20.2
	<i>5.8</i>	<i>5.7</i>	<i>13.7</i>	<i>12.6</i>	<i>7.4</i>	<i>7.1</i>	<i>79.4</i>	<i>30</i>
Sugar maple	1.60	2.75	0.02	0.64	1.54	2.20	0.30	0.9
	<i>11.0</i>	<i>10.1</i>	<i>131.2</i>	<i>40.1</i>	<i>7.8</i>	<i>16.5</i>	<i>23.4</i>	<i>64</i>
Copaiba	13.16	17.60	0.43	12.26	8.03	20.73	0.97	3.4
	<i>29.8</i>	<i>21.8</i>	<i>48.2</i>	<i>37.4</i>	<i>8.4</i>	<i>23.2</i>	<i>15.8</i>	<i>61</i>
Palisangre negro	5.11	9.46	0.42	3.76	7.27	11.45	0.84	9.5
	<i>11.5</i>	<i>17.7</i>	<i>25.3</i>	<i>33.2</i>	<i>11.9</i>	<i>18.2</i>	<i>13.4</i>	<i>47</i>
Estoraque	3.35	7.75	0.54	3.41	3.93	7.88	0.70	5.3
	<i>10.7</i>	<i>11.8</i>	<i>35.7</i>	<i>29.1</i>	<i>4.0</i>	<i>14.3</i>	<i>9.5</i>	<i>17</i>
Tahuarí	2.55	4.15	1.11	1.56	2.33	5.01	0.35	5.3
	<i>12.6</i>	<i>9.2</i>	<i>25.1</i>	<i>18.5</i>	<i>11.1</i>	<i>13.1</i>	<i>7.3</i>	<i>49</i>
Palosangre	4.24	9.50	3.72	10.54	3.87	18.13	0.55	10.4
	<i>14.1</i>	<i>18.9</i>	<i>23.2</i>	<i>39.9</i>	<i>11.7</i>	<i>21.2</i>	<i>9.8</i>	<i>33</i>

ranged from 3° in caoba to 20° in pumaquiro. High within-species variation in interlocked grain of ishpingo and pumaquiro woods has been previously reported by Hernández and Almeida (2003).

As previously indicated, two types of matched samples were used for the parallel and tangential compression tests (Hernández 2006). A comparison between such types of samples showed similar EMC values for the three common moisture conditions that were studied (Table 3). In contrast, EMC estimates varied consistently among species for all moisture sorption conditions. Variations in EMC among species have already been reported (Near 1955; Higgins 1957; Spalt 1958; Choong and Achmadi 1991; Nzokou and Kamdem 2004). Moreover, EMC exhibited a very low within-species variation for all woods studied (Table 3). Thus, precise EMC values are obtained when hygrothermal conditions are carefully maintained during sorption. Species played an important role with respect to variation in EMC, which was greatest in ish-

pingo negro, palisangre negro, and palosangre (Table 3). These species also were among those having the highest concentrations of extractives (Table 2). Sugar maple and cedro had lower concentrations of wood extractives, and were among those species exhibiting less variability in EMC.

### Exploratory analysis

Regression of the EMC responses required exclusion of some data from the analyses. Consequently, the global analysis included only nine woods with ninety samples. Copaiba wood was removed given that this species showed atypical sorption behavior (Fig. 2). Furthermore, the tangential samples of ishpingo negro that underwent desorption at 58% RH (d58T) yielded somewhat erratic results for EMC (Table 3), and therefore also were not used in the global analysis. This group (d58T) was therefore studied with only eighty samples.

The five regression models of the exploratory

TABLE 3. Equilibrium moisture content (EMC) for all woods as a function of sorption conditions at 25°C. Means (percentage) and coefficients of variation (percentage of means, in italics).

Wood species	First adsorption			Second desorption		
	33% RH	76% RH		58% RH		33% RH
	PS <sup>1</sup> a33P	PS <sup>1</sup> a76P	TS <sup>1</sup> a76T	PS d58P	TS d58T	PS d33P
Caoba	5.79	12.83	12.91	12.47	12.53	8.01
	<i>1.2</i>	<i>1.3</i>	<i>0.9</i>	<i>0.5</i>	<i>0.6</i>	<i>1.1</i>
Cedro	5.61	13.03	12.84	11.94	11.98	7.45
	<i>0.7</i>	<i>0.5</i>	<i>0.9</i>	<i>0.7</i>	<i>1.1</i>	<i>1.7</i>
Ishpingo negro	3.44	9.41	9.51	8.58	(6.90) <sup>2</sup>	5.43
	<i>3.7</i>	<i>1.7</i>	<i>1.7</i>	<i>2.4</i>	<i>4.2</i>	<i>2.2</i>
Pumaquiro	4.44	11.60	11.43	11.14	11.18	6.85
	<i>0.8</i>	<i>0.4</i>	<i>0.4</i>	<i>0.4</i>	<i>0.2</i>	<i>0.7</i>
Sugar maple	5.04	13.20	13.15	11.67	11.74	7.00
	<i>0.5</i>	<i>0.4</i>	<i>0.6</i>	<i>1.6</i>	<i>1.1</i>	<i>1.5</i>
Copaiba	5.70	12.93	12.96	13.01	13.01	8.22
	<i>0.7</i>	<i>1.1</i>	<i>1.5</i>	<i>3.4</i>	<i>3.4</i>	<i>3.3</i>
Palisangre negro	4.69	11.28	11.19	10.84	10.57	6.83
	<i>4.8</i>	<i>4.4</i>	<i>4.1</i>	<i>3.4</i>	<i>4.6</i>	<i>1.7</i>
Estoraque	4.80	11.36	11.47	10.89	10.81	6.95
	<i>2.6</i>	<i>1.9</i>	<i>1.8</i>	<i>1.6</i>	<i>2.0</i>	<i>1.7</i>
Tahuarí	4.97	11.91	11.98	11.34	11.42	6.83
	<i>1.9</i>	<i>1.7</i>	<i>1.6</i>	<i>1.9</i>	<i>2.1</i>	<i>2.8</i>
Palosangre	3.74	9.58	9.78	9.36	9.30	5.79
	<i>10.1</i>	<i>7.9</i>	<i>5.8</i>	<i>6.8</i>	<i>5.4</i>	<i>4.4</i>

<sup>1</sup> PS Parallel sample; TS: Tangential sample

<sup>2</sup> Erratic results

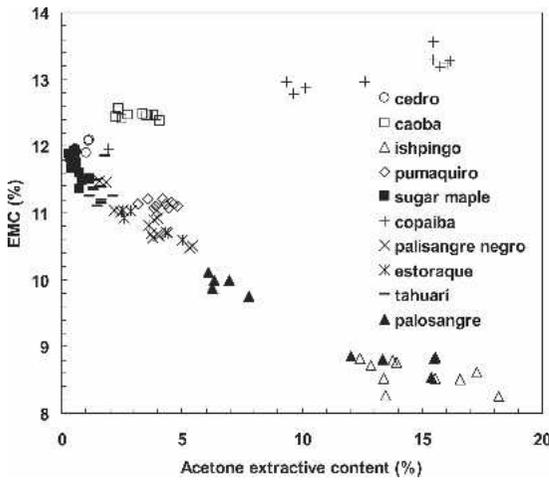


FIG. 2. Equilibrium moisture content in desorption over 58% relative humidity and 25°C for all woods studied as a function of their acetone extractives. Parallel samples.

analysis were evaluated in terms of their coefficients of determination ( $R^2$ ) and CV (not shown). All models used to explain EMC variation were statistically significant at the 0.01 probability level. However, EMC was sensitive to the different models used. Model 4, which included the substances soluble in organic solvents taken separately, best explained the variation in EMC (from 85% to 97% of the total variation in EMC, depending on the moisture sorption condition studied). Model 1, which in-

cluded the substances soluble in cold water, gave the lowest correlations (from 41% to 70% of the total variation in EMC).

Therefore, only Model 4 will be considered in the following discussion. It is clear that a kind of study for tropical hardwoods based on extractions using either cold or hot water as solvents would not give such good results. The EMC results were clearly affected by the substances soluble in organic solvents present in these woods.

### Equilibrium moisture content

EMC clearly varied among the different woods placed under the same moisture sorption conditions at 25°C (Table 3). The results indicated that the equilibrium moisture contents were more scattered near 100% RH (not shown). Control of the sample mass taken during sorption at this condition made it possible to notice the particular behavior of four of the ten species studied. For this reason, the variation in adsorption over distilled water will be discussed elsewhere (Hernández 2007b).

The multiple linear regression equations of EMC for all moisture conditions are given in Table 4. To evaluate the relative importance of each independent variable on EMC variation, the regression coefficients were standardized by

TABLE 4. Regression equations of the equilibrium moisture content (EMC) at 25°C as a function of corrected oven-dry density ( $D_{oc}$ ), interlocked grain (IG), ash content (ASH), as well as extractives obtained successively in cyclohexane (CYC), acetone (ACE), and methanol (MET)<sup>1</sup>.

Moisture sorption condition <sup>2</sup>	Equations	R <sup>2</sup> (%)	CV (%)
a33P	EMC = 6.1 - 0.14 ACE - 1.30 $D_{oc}$ + 0.36 ASH - 0.016 IG (-0.90) (-0.28) (0.15) (-0.14)	92.1	4.6
d33P	EMC = 8.4 - 0.15 ACE - 1.67 $D_{oc}$ + 0.081 MET - 0.014 IG (-0.94) (-0.35) (0.20) (-0.12)	84.6	4.4
d58P	EMC = 13.4 - 0.23 ACE - 2.06 $D_{oc}$ - 0.012 IG (-0.94) (-0.27) (-0.07)	90.7	3.4
d58T	EMC = 14.3 - 0.19 ACE - 3.05 $D_{oc}$ - 0.023 IG - 0.44 ASH (-0.66) (-0.48) (-0.16) (-0.14)	85.5	3.4
a76P	EMC = 15.5 - 0.21 ACE - 3.19 $D_{oc}$ - 0.037 IG - 0.12 CYC - 0.37 ASH - 0.05 MET (-0.77) (-0.38) (-0.18) (-0.12) (-0.09) (-0.07)	97.1	2.1
a76T	EMC = 15.2 - 0.19 ACE - 2.79 $D_{oc}$ - 0.049 IG - 0.40 ASH - 0.10 CYC - 0.05 MET (-0.73) (-0.35) (-0.25) (-0.11) (-0.10) (-0.08)	95.3	2.5

<sup>1</sup> The terms in parentheses are the beta coefficients of the regression.

<sup>2</sup> First letter: a = adsorption, d = desorption; number = RH in percent; last letter: P = parallel samples, T = tangential samples.

calculating the beta coefficients. These coefficients were calculated for each individual regression, and therefore, they are not comparable from one moisture sorption condition to another. On the other hand, the order of importance of each variable was verified by systematic elimination of the more influential points of measurement, which were chosen from Cook's distances (Draper and Smith 1981).

The models that were retained in the analyses explained 85% to 97% of the variation in EMC (Table 4). The low coefficients of variation (from 2% to 5%) suggest that these equations may be used for predictive purposes. The three most important independent variables in the models were the acetone extractives, the corrected oven-dry density, and the interlocked grain, which were negatively related to EMC. For all moisture sorption conditions, the acetone fraction (ACE) was by far the most important variable affecting EMC in the tropical hardwoods, but its relative influence on EMC decreased as RH increased. Examination of the standardized regression coefficients show that ACE accounted for about 60% of the total variance-explained by multiple regression under the 33% RH condition (regressions of a33P and d33P groups were pooled, Table 4). This contribution decreased to about 46% under the 76% RH condition (regressions of a76P and a76T groups were pooled, Table 4).

The effect of the acetone fraction on EMC of parallel samples following desorption at 58% RH (d58P) is illustrated in Fig. 2. Results for copaiba are also shown, even though they were not included in the regression analysis. It is evident that this wood deviates from the global trend since its acetone extractives contribute to increasing the EMC instead of decreasing it (Fig. 2). The hygroscopicity of copaiba can be explained by the hydrophilic nature of the acetone extractives and/or by their location and distribution within the cell walls. The first alternative appears more plausible than the second, given that such substances did not increase the swelling of this wood (Hernández 2007a). The acetone extractives of caoba could also have a similar effect, although they were included in

the regression analysis since their effects on regression results were negligible. The results obtained by Cooper (1974) for black walnut and by Venäläinen et al. (2006) for Siberian larch may also merit this type of explanation.

Ishpingo negro contains high proportions of acetone extractives (14.7%), which have a hydrophobic effect on EMC (Fig. 2). Given that this species was not included in the regression for the desorption over 58% RH (d58T), the relative influence of the independent variables on EMC variation was altered (Table 4). Therefore, the wood species and their number have an important influence on this type of research, at least until the nature and role of extractives can be better understood.

An interesting aspect of the EMC variation is shown in Fig. 3. As for the oven-dry density, it is possible to define a "corrected EMC" ( $EMC_c$ ) as follows:

$$EMC_c = \frac{M_{H_2O}}{M_{OC}} = \frac{M_H - M_O}{M_O - M_C} \cong \frac{M_H - M_O}{M_O(1 - e)} = \frac{EMC}{1 - e} \quad (2)$$

where  $M_{H_2O}$  denotes the mass of free and bound

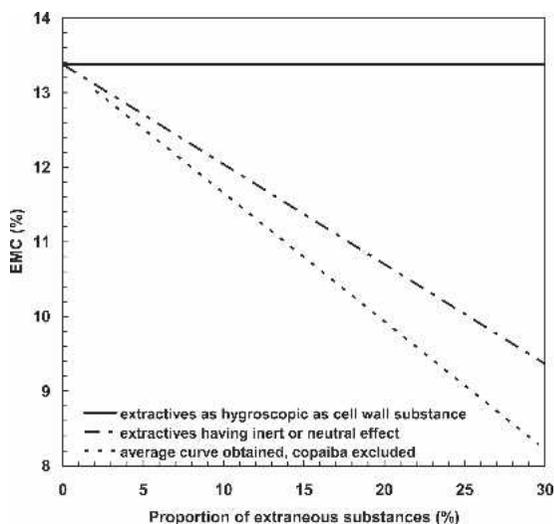


FIG. 3. Hygroscopicity of the extraneous substances and equilibrium moisture content of wood. Parallel samples equilibrated in adsorption over 76% relative humidity and 25°C.

water,  $M_H$  is the mass of the sample including water, and  $M_C$  is the total mass of the extraneous substances. This corrected  $EMC_c$  is therefore reported to the cell-wall substance alone, without taking other wood components into account.  $EMC$  is related to  $EMC_c$  as follows:

$$EMC = EMC_c(1 - e) = EMC_c - EMC_c e \quad (3)$$

This is a linear equation where  $EMC_c$  can represent a constant in relation to the amount of extraneous substances. This relationship is shown as a dot dash line in Fig. 3. This line represents the values that  $EMC$  should have if the extraneous substances had an inert character (adding only mass to wood). Consequently, depending on whether these compounds exhibit either a hydrophobic or a hydrophilic effect, the measured  $EMC$  must be located under or above this dot dash line. Therefore, the lowest average line (dash line) shown confirms that wood extractives have principally a global hydrophobic effect.

A summary of the multiple linear regression analysis for  $EMC_c$  is presented in Table 5. The retained models explained from 94% to 99% of the total variation in  $EMC_c$ . The relationships were hence stronger for  $EMC_c$  than for  $EMC$ . The very low coefficients of variation (from 2% to 4%) suggest that these equations can be used

for prediction. The signs of the regression coefficients confirm the negative role played for all independent variables on  $EMC$ .  $EMC$  decreased as acetone-extracted fraction, wood density, and interlocked grain increased. This was not so clearly established when the uncorrected  $EMC$  variation was analyzed. The acetone fraction was again the most important variable of the models retained.

The cyclohexane and methanol fractions also participate but to a lesser degree in  $EMC$  variation (Tables 4 and 5). These substances are located within wood to both opposite sides of acetone extractives in regards to their polarity. This could be the same for their accessibility to cell walls if the interpretation of Morgan and Orsler (1969) is considered. Cyclohexane is a non-polar solvent and probably incapable of opening up and penetrating cell walls. This solvent would be expected to remove the extractable material located within the cell lumina and intercellular spaces. These substances appeared to have a neutral or inert effect on  $EMC$  (adding only mass to wood as shown in Fig. 3) because they affected neither the swelling nor the compressive properties of tropical hardwoods under study (Hernández 2006b, 2006c). In contrast, acetone and methanol are polar solvents that can swell wood structure. When used for extraction, these solvents would remove material from

TABLE 5. Regression equations of the corrected equilibrium moisture content ( $EMC_c$ ) at 25°C as a function of corrected oven-dry density ( $D_{oc}$ ), interlocked grain (IG), ash content (ASH), as well as extractives obtained successively in cyclohexane (CYC), acetone (ACE), and methanol (MET)<sup>1</sup>.

Moisture sorption condition <sup>2</sup>	Equations	R <sup>2</sup> (%)	CV (%)
a33P	$EMC_c = 6.0 - 0.17 ACE - 1.2 D_{oc} - 0.018 IG - 0.04 MET + 0.20 ASH$ (-0.90) (-0.22) (-0.13) (-0.07) (0.07)	96.0	4.4
d33P	$EMC_c = 8.2 - 0.18 ACE - 1.5 D_{oc} - 0.10 CYC - 0.014 IG$ (-0.85) (-0.24) (-0.14) (-0.09)	93.9	4.2
d58P	$EMC_c = 13.5 - 0.29 ACE - 2.2 D_{oc} - 0.024 IG - 0.12 CYC - 0.46 ASH - 0.07 MET$ (-0.84) (-0.21) (-0.10) (-0.09) (-0.09) (-0.07)	96.9	3.1
d58T	$EMC_c = 14.0 - 0.26 ACE - 2.8 D_{oc} - 0.11 MET - 0.025 IG - 0.54 ASH - 0.11 CYC$ (-0.68) (-0.32) (-0.16) (-0.13) (-0.13) (-0.10)	94.1	3.2
a76P	$EMC_c = 15.2 - 0.28 ACE - 2.9 D_{oc} - 0.19 MET - 0.24 CYC - 0.038 IG - 0.43 ASH$ (-0.71) (-0.25) (-0.18) (-0.18) (-0.13) (-0.07)	98.7	2.1
a76T	$EMC_c = 15.0 - 0.26 ACE - 2.6 D_{oc} - 0.18 MET - 0.048 IG - 0.22 CYC - 0.46 ASH$ (-0.69) (-0.22) (-0.19) (-0.17) (-0.16) (-0.08)	98.1	2.5

<sup>1</sup> The terms in parentheses are the beta coefficients of the regression.

<sup>2</sup> First letter: a = adsorption, d = desorption; number = RH in percent; last letter: P = parallel samples, T = tangential samples.

within the wall structure. On the other hand, the effect of the inorganic substances (ash content) on EMC appeared to be very small.

Wood density, and to a lesser degree interlocked grain, exhibit a negative relationship with EMC (Tables 4 and 5). Barkas (1949) established that stress levels in wood likely participate in this equilibrium. Compression stresses decrease EMC while tension stresses increase it. Interlocked grain likely exerts external stresses while wood density indicates the level of internal stresses. The effect of both stresses would be manifested even until the equilibrium of moisture sorption. Another interpretation is that the degree of cellulose crystallinity increases with the wood density, which would decrease the number of sorption sites (El-Osta 1971). The negative effects of the degree of cellulose crystallinity and wood density on EMC have been reported by Wang and Cho (1993).

#### *Hygroscopicity parameters*

The sorption ratio (S) was proposed by Noack et al. (1973) to characterize the sensitivity of changes in EMC ( $\Delta\text{EMC}$ ) to changes in RH ( $\Delta\text{RH}$ ) and is defined as:

$$S = \frac{\Delta\text{EMC}}{\Delta\text{RH}} \quad (4)$$

This parameter assumes a linear relationship between EMC and RH. Values of S thus were

calculated for adsorption between 33% and 76% RH, and for desorption between 33% and 58% RH. This was done by combining the values of parallel samples coming from the same initial board. From these analyses, sugar maple was found to be the most sensitive to changes in RH (Table 6). Copaiba wood, whose acetone extractives play a hydrophilic role, closely followed the behavior of sugar maple. In contrast, the EMC of wood species containing high extractives contents, as ishpingo negro and palosangre, was less affected by changes in RH (Table 6).

The variables affecting the sorption ratio S were analyzed by stepwise multiple regression. The analysis presented in Table 7 indicates that the retained models explained from 90% to 93% of the total variation in S. Again, low coefficients of variation (3.4%) suggest that these equations can be used for prediction. The substances soluble in acetone were those contributing more to the hygroscopic stability. The standardized or beta coefficients from multiple regressions showed that acetone extractives accounted for about 25% (adsorption) and 56% (desorption) of the variation in S. Simple linear regression of S under desorption against the acetone fraction highlights this global tendency (Fig. 4). Results of copaiba wood that were not included in the regression are also depicted for comparative purposes. Acetone extractives appear to give hygroscopic instability to this wood. Further investigation with more samples is needed to validate these results.

TABLE 6. Ratio of sorption S and sorption hysteresis parameters at 25°C for the parallel samples.

Wood species	Ratio of sorption S		Sorption hysteresis parameters <sup>1</sup>	
	Adsorption from 33% to 76% RH (%EMC/%RH)	Desorption from 58% to 33% RH (%EMC/%RH)	Hysteresis ratio	Hyst (%)
Caoba	0.166	0.178	0.72	2.22
Cedro	0.174	0.180	0.75	1.84
Ishpingo negro	0.141	0.126	0.63	1.99
Pumaquiro	0.168	0.172	0.65	2.41
Sugar maple	0.192	0.187	0.72	1.96
Copaiba	0.170	0.192	0.69	2.59
Palisangre negro	0.155	0.161	0.69	2.14
Estoraque	0.154	0.158	0.69	2.15
Tahuarí	0.163	0.180	0.73	1.86
Palosangre	0.137	0.143	0.65	2.05

<sup>1</sup> Estimated at 33% relative humidity

TABLE 7. Regression equations of the ratio of sorption *S* as a function of corrected oven-dry density (*D<sub>oc</sub>*), interlocked grain (IG), ash content (ASH), as well as extractives obtained successively in cyclohexane (CYC), acetone (ACE), and methanol (MET). *Copaiba* wood was not included<sup>1</sup>.

Regression equations	R <sup>2</sup> (%)	CV (%)
S in adsorption (33% to 76% RH) $S = 0.221 - 0.0016 \text{ ACE} - 0.044 \text{ D}_{oc} - 0.016 \text{ ASH} - 0.0032 \text{ CYC} - 0.00050 \text{ IG} - 0.0016 \text{ MET}$ (-0.46)            (-0.42)            (-0.31)            (-0.29)            (-0.20)            (-0.18)	89.5	3.4
S in desorption (58% to 33% RH) $S = 0.214 - 0.0040 \text{ ACE} - 0.019 \text{ ASH} - 0.0028 \text{ D}_{oc} - 0.00040 \text{ IG} - 0.0016 \text{ CYC}$ (-0.94)            (-0.29)            (-0.22)            (-0.13)            (-0.11)	92.8	3.4

<sup>1</sup> The terms in parentheses are the beta coefficients of the regression.

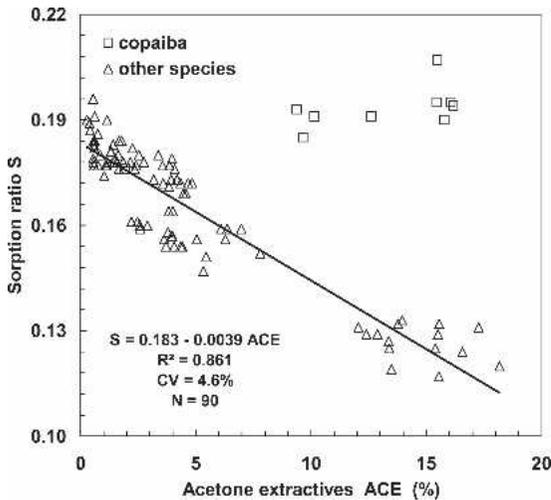


FIG. 4. Sorption ratio *S* under desorption at 25°C and between 33% and 58% relative humidity as a function of the acetone extractives.

The sorption isotherm hysteresis is usually evaluated by the “hysteresis ratio,” which is defined as the EMC at adsorption divided by EMC at desorption for a given RH. Spalt (1958) posited that wood extractives could have an important effect on this ratio. However, Wangaard and Granados (1967) detected contradictory effects of the extraction treatment on this parameter. This definition implies that if both EMCs are affected by a same ΔEMC, the hysteresis ratio will be dependent on this ΔEMC. It follows that the sorption hysteresis was also evaluated here as the difference between the two isotherms for a given RH, so-called “Hyst”, as follows:

$$\text{Hyst} = (\text{EMC}_{\text{des}} - \text{EMC}_{\text{ads}})_{\text{RH}} \quad (5)$$

The hysteresis ratio and the “Hyst” parameters that were calculated for 33% RH are shown in Table 6. Ambiguous results are obtained when comparing both criteria of evaluation. Regression analysis performed for both parameters showed that there is no dominant factor among those studied for explaining the hysteresis variation. Therefore, the extent of the sorption hysteresis is related to other parameters of hygroscopicity, which are typical to each individual species. The contradictions reported in the literature concerning this subject probably find here some explanation.

SUMMARY AND CONCLUSIONS

Experiments of cold-water and hot-water solubilities, sequential extractions with cyclohexane, acetone, and methanol solvents, ash determination, wood density, as well as interlocked grain measurements, were conducted with nine tropical hardwoods and sugar maple wood. Results of these measurements were associated with those of moisture sorption properties obtained from unextracted but matched samples using a multiple step procedure at 25°C. The main conclusions of this work may be summarized as follows:

1. There was high variation in wood extractives, interlocked grain, EMC, and hygroscopic stability within and among these wood species.
2. Sequential extraction with organic solvents was the most suitable method for evaluating the effect of extractives on sorption behavior of tropical hardwoods.

3. The cyclohexane-extracted fraction exerted little effect on EMC of inert nature.
4. The acetone fraction of wood extractives was the most significant variable affecting EMC and hygroscopic stability of tropical hardwoods under study. In general, EMC decreased and hygroscopic stability increased as acetone extractives content increased. The influence of these compounds on EMC decreased as relative humidity increased. However, compounds soluble in this solvent would play a hydrophilic role for copaiba and, probably, caoba woods.
5. The methanol extracted fraction had a significant but negligible effect on the sorption behavior of these wood species.
6. EMC also decreased as wood density and interlocked grain increased.

#### ACKNOWLEDGMENTS

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