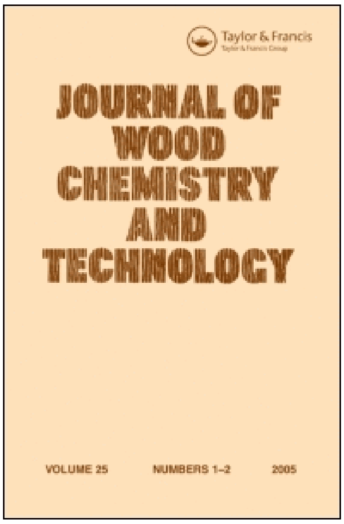

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Estimation of Jack Pine, Black Spruce, and Balsam Fir Proportions in Wood Chips

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ABSTRACT

This article outlines an analytical approach which can be used to evaluate the relative proportions of jack pine, black spruce, and balsam fir in wood chips. The evaluation is made possible through the presence of species-specific natural products (markers) in the softwoods studied. Calibration curves were drawn and applied to evaluate the proportion of these species in a laboratory prepared sample of wood chips.

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INTRODUCTION

Black spruce (*Picea mariana*), balsam fir (*Abies balsamea*), and jack pine (*Pinus banksiana*) are three of the softwoods most utilized in pulp and paper manufacture in eastern Canada.[1] Pulp and paper industries do not favor incorporation of jack pine in the pulp since it can lead to increased power consumption in paper making as well as to paper yellowing.[1–3] For these reasons, pulp and paper firms wish to limit the presence of jack pine in the pulp and favor its use as timber. In practice, paper mills obtain their wood chips from sawmills as a mixture of the three aforementioned species in variable proportions. With process optimization and paper quality control in mind, it is important for the mills to be aware of these proportions. Several methods have been studied to differentiate the wood of conifers, and in certain cases attempts have made to apply such methods to sorting lumber.[4–8] However, these methods have not been applied to a mixture of wood chips. To the best of our knowledge, only one other analytical approach has been reported by Finnish researchers[2] on the evaluation of pine (*Pinus silvestris*) and spruce (*Picea abies*) proportions in mechanical pulping. The aim of this work was to develop and validate an analytical approach which would eventually lead to an evaluation of the relative amounts of each species in a wood chip sample through the use of species-specific molecular markers.

EXPERIMENTAL

Wood

Twelve jack pines, twelve balsam firs, and ten black spruces, growing in the Saguenay-Lac-St-Jean region of Quebec, were felled in August 1995. The age of the trees varied from 24 to 114 years for black spruce, 55 to 102 years for jack pine, and 35 to 122 years for balsam fir. Wood disks (1 cm) were cut from debarked logs (first two meters of the stem) of each tree and the sapwood and heartwood were carefully separated using chisels. Pieces of heartwood and sapwood were dried overnight at room temperature and ground with an industrial grinder equipped with a 2 mm sieve. Equivalent amounts of sapwood from each log of a particular species were mixed together in order to minimize individual variations. Heartwood mixtures were prepared in the same fashion. Since the composition of wood chips from sawmills is about 75% sapwood and 25% heartwood, the mixtures used for analyzis contained the same proportions. Calibration curves were obtained using ten ternary mixtures with different amount of the three wood species. The percentage of black spruce in the mixtures varied from 60 to 95% and those of balsam fir and jack pine were between 0 and 25%, since in eastern Canada chips are composed mainly of black spruce (generally more than 65%).

Bark

Bark of three black spruces, three balsam firs, and three jack pines were took, extracted the same way as wood and analyzed by GC.

Extraction

Samples of the wood mixture (50 g) were extracted with 295 mL of hexane and 5 mL of a solution of an internal standard (1.5 g tetradecane in 500 mL of hexane). We choose to work with hexane because it is a good solvent to extract the volatiles products of low polarity, which can then be analyzed easily by GC. The mixture of wood and solvent was slowly stirred for 10 min at room temperature using a mixer, and an aliquot of 20 mL was taken from the supernatant solution, dried over anhydrous $MgSO_4$, filtered, and evaporated at room temperature to 0.5 mL.

Gas Chromatographic (GC) Analyses of Wood Extracts

Gas chromatographic analyzes were performed on a Hewlett-Packard 5890 gas chromatograph equipped with a polar Supelcowax column (30 m × 0.25 mm with 0.25 μm film) and an apolar DB-5 column (30 m × 0.25 mm with 0.25 μm film) and a split-splitless injection port (split mode). The temperature program was 60°C for 2 min, then 2°C/min to 140°C, then 1°C/min to 190°C, then 2°C/min to 210°C, and this temperature was held constant for 28 min. The specific markers were identified by their Kovats indices[9] on both columns and by spectroscopic analyzes.[10]

Impact of Aging on Chemical Markers Content in Wood Chips

A large sample (6–7 m^3) of chips produced by a sawmill was stored on the grounds of a pulp and paper mill for a 2 month period (from early

September to early November). During this period the temperature varied from 15 to -5°C. Four samples were withdrawn, three of these during the first month and one at the end of the two month period. Samples were extracted and the amount of markers measured.

RESULTS AND DISCUSSION

Chemical Marker Selection

Previous work[10] on the chemical differences between these softwoods enabled identification of natural products specific to balsam fir and jack pine but not to black spruce. Chemical marker selection was done in such a way as to satisfy certain criteria. First, an extractive is species specific, i.e., is a marker, if it is found only in the extract of this species, or, if it is abundant in the extract of one species and at very low concentrations in the others. Second, the concentration of the marker has to be sufficient to exclude sensitivity problems in the analytical method. Chemical extractives selected as markers were juvabione[11–12] found in balsam fir wood, and pimaral[10] found in jack pine wood. The gas chromatographic analyzes of the bark of the three species showed that these markers are not present in the bark, only in the wood. Figure 1 shows three typical chromatograms of extracts for the three softwood species. Tables 1 and 2 show the percentage composition of the markers in the heartwood and the sapwood of these conifers. Juvabione is quite abundant in balsam fir extracts and is totally absent in the extracts of the two other species. In the case of jack pine, the diterpene marker is less abundant than juvabione in balsam fir, but still present in adequate quantities to be used as a marker. It is also present in black spruce, but in trace quantities only. Thus, although we have not identified a species specific marker for black spruce, under the present conditions of extraction and analyzis, the relative proportion of black spruce in the chip pile can still be evaluated, not directly, but by taking into account the known proportions of fir and pine. The presence in the sample of a sizable proportion of a species other than these three softwoods, such as a hardwood, would invalidate this approach.

Calibration Curves

The amounts of jack pine and balsam fir markers in extracts of ternary mixtures were measured by gas chromatography. The amount

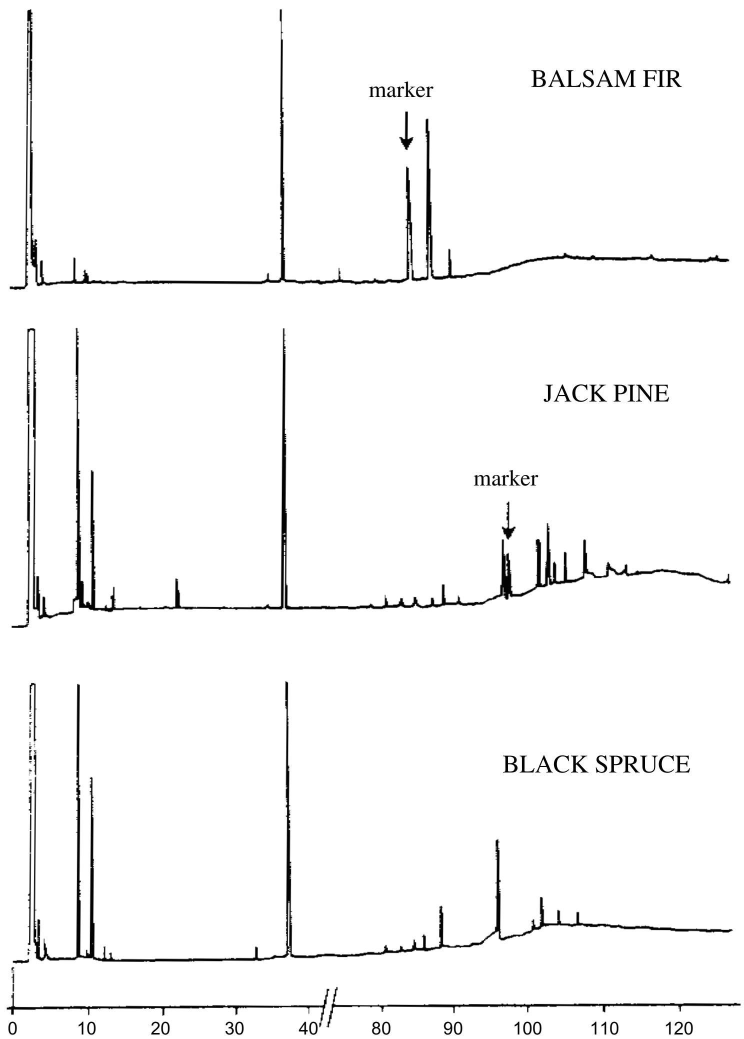

Figure 1. Schematic gas capillary chromatograms of the extracts of wood of balsam fir, jack pine, and black spruce.

of each marker was quantified as the ratio of the chromatographic peak area of the marker relative to that of an internal standard (IS). Each extract was injected at least twice, and mean values were used to create calibration curves. Chromatograms of repeated injections of the same ternary mixture extract were quite reproducible (% variation of each

Table 1. Percentage of markers present in the heartwood of three species of conifers.

Identification	Retention indices on DB-5 column	Composition (%)		
		Jack pine	Black spruce	Balsam fir
Juvabione	2017	0	0	55.44
Pimaral	2158	6.43	0.74	0

Table 2. Percentage of markers present in the sapwood of three species of conifers.

Identification	Retention indices on DB-5 column	Composition (%)		
		Jack pine	Black spruce	Balsam fir
Juvabione	2017	0	0	15.44
Pimaral	2158	9.66	0.77	0

peak was less than 5%). Calibration curves show good linearity, as can be seen in Figs. 2 and 3. It should be noted that the calibration curve for jack pine (Fig. 3) does not pass through the origin because the jack pine marker is present in trace quantities in the wood of black spruce. These calibration curves permit evaluation of the proportions of jack pine and balsam fir in samples of wood chips simply by doing an extraction with hexane and analyzing the extract by GC. As an example of the precision of our analytical method, a wood sample, prepared in our laboratory by mixing a predetermined proportion of the three conifers, was extracted with hexane. Gas chromatographic analyzis showed the presence of the balsam fir marker (juvabione area/IS area = 0.07) and the jack pine marker (pimaral area/IS area = 0.023). Using Figs. 2 and 3, interpolation gave the results shown in Table 3. The uncertainties of the measurements shown in Table 3 were determined with the standard error of the estimate[13] at a confidence level of 95% (twice the standard error of the estimated value). As seen in Table 3, percentages measured for jack pine and balsam fir are not far removed from the actual values.

Also, the accuracy of the measurement of the relative proportions of the species is very dependent on the proportions of heartwood and sapwood, which are estimated at 25:75 by certain industries. If this ratio

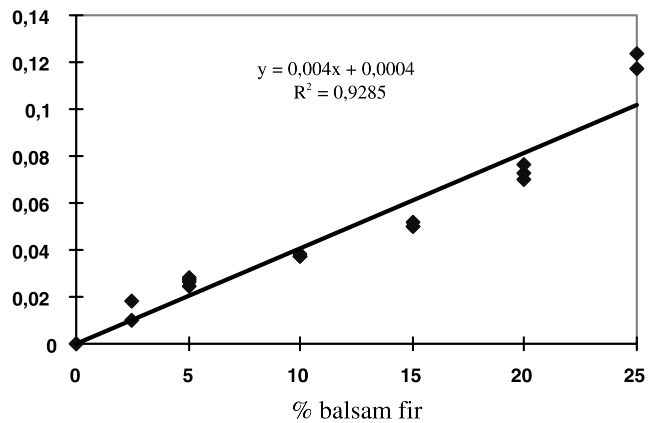

Figure 2. Calibration curve for balsam fir.

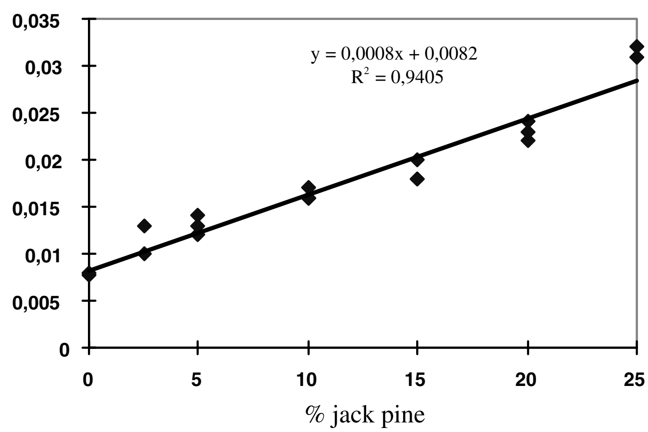

Figure 3. Calibration curve for jack pine.

Table 3. Actual and measured proportions of wood of the three conifers in a laboratory-prepared sample.

	Jack pine	Balsam fir	Black spruce
Actual proportions (%)	20	20	60
Measured proportions (%)	18.5 ± 4.1	17.4 ± 4.8	64.1

Table 4. Percentage variation of specific markers as a function of time.

Aging (days)	Jack pine (%)	Balsam fir (%)
1	6	51
15	6	38
30	7	40
60	6	39

changes, the reliability will decrease rapidly as the quantity of markers in heartwood and sapwood are different. Furthermore, the use of a limited number of trees in this study, twelve jack pines, twelve balsam firs, and ten black spruces, to minimize the effect of individual variations within a single species, does not guarantee that the sample used is a representative of the species. To minimize further the level of this uncertainty, it would have been necessary to use a much larger sample of individual trees for establishing the calibration curves; this would be a daunting task considering the number of trees that may be required. Analysis of a large number of trees to know the individual variation in the chemical composition, especially the markers, is a work we plan to do later to complete our study.

Impact of Aging on Wood Chips

Normally, as many industries told us, wood chips do not stay outside the mill more than 3 weeks. In spite of this, we wanted to study the effect of aging (temperature, humidity, etc.) on the chemical marker concentration in industrial wood chips. As shown in Table 4, the marker concentration in the wood material was only weakly influenced by aging: only a decrease in the amount of balsam fir marker was observed after two weeks. This suggests that, with normal storing conditions, species specific markers are sufficiently stable to be used for analytical purposes. It would be interesting to see if the effect of aging is more important during the summer period when the temperature vary from 15 to 30°C.

CONCLUSION

As has been shown in this work at the laboratory level, it is possible to evaluate the proportions of jack pine and balsam fir in a mixture of wood chips, as well as black spruce by difference, by taking advantage of the presence of species specific natural products in the wood. Calibration curves were established using mixtures of wood chips of different proportions of the three conifers and in a ratio of heartwood to sapwood of 25 to 75, similar to that produced by sawmills. The accuracy of the method depends on the ratio of heartwood to sapwood. Finally, chip aging when the temperature varied from −5 to 15°C did not have a large influence on the concentrations of markers. Further work is in progress to improve the accuracy and precision of the method by examining peak ratios and by sampling a larger number of trees.

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