Gas chromatographic analysis of acetone extractives in lodgepole pine and western hemlock thermomechanical pulp furnish

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ABSTRACT: We analyzed acetone extractives in western hemlock and lodgepole pine thermomechanical pulp (TMP) furnishes using a combination of low resolution gas chromatography (LRGC) and high resolution gas chromatography (HRGC). The analytical scheme developed was rapid and repeatable. It provided detailed data about extractives component classes as well as individual compounds. Extracts of western hemlock furnish were composed primarily of lignans. Extractives in lodgepole pine were mostly lipophilic, although a significant polar fraction included lignans, oxidized resin acids, flavonoids and stilbenes.

These findings are significant because scientists, engineers, and mill managers involved in TMP manufacturing increasingly need to understand the composition and behavior of various classes of wood extractives at various stages of production. This knowledge leads to effective solutions regarding TMP quality, water usage, chemical consumption, paper sizing, and mill-machine runnability. We also used the methods outlined in this paper to analyze wood extractives in TMP and newsprint at various stages of production..

Application: This paper describes a practical system for rapidly identifying a wide range of wood extractives in TMP furnish.

Improved methods of water system closure in thermomechanical pulp (TMP) mills rely on understanding the behavior of resin and other wood components released from fibers during thermomechanical pulping. Release of resin and other extractives from fibers during pulping, bleaching, and newsprint manufacture significantly impacts water recycling efforts and leads to increased waste water treatment demands. Wood resin retained on fibers can potentially self-size TMP and reduces requirements for synthetic paper-sizing agents.

To better describe the behavior of wood extractives during thermomechanical pulping, we developed quantitative methods for analysis of extractives present in various TMP process streams. This paper describes the application of these methods to the extractives in western hemlock (*Tsuga heterophylla*) and lodgepole pine (*Pinus contorta*) TMP furnish. The methods are based on both low-resolution gas chromatography (LRGC) and high-resolution gas chromatography (HRGC).

GC analysis of extractives

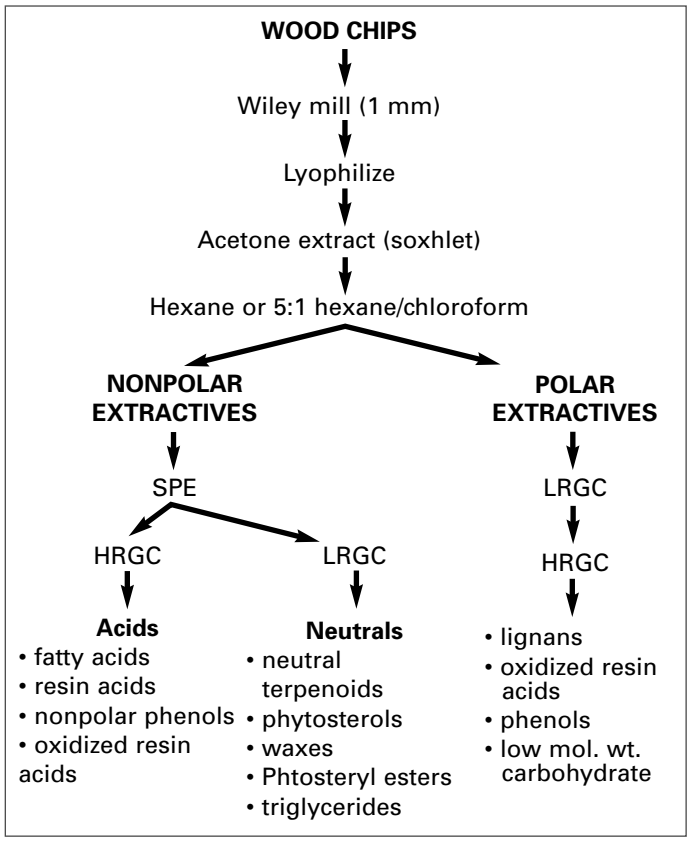
A wide range of common wood extractives can be conveniently analyzed using gas chromatography (GC). Modern GC techniques include safe and efficient derivatization methods, specialized capillary columns, and rapid identification of individual components by mass spectrometry. Additionally, temperature-programmable on-column injection (POC) makes it possible to characterize relatively nonvolatile extractives. We can, for example, profile mixed triglycerides and steryl-esters with high resolution using POC [1-5]. Previously, fatty acid esters were hydrolyzed before GC analysis, so those assays would require more time.

Initially, attempts to profile nonpolar wood extractives without hydrolysis involved the use of packed columns [6, 7]. This approach simplified sample preparation in exchange for low resolution and long run times. Shorter run times and improved resolution have been achieved using short wide-bore capillary columns and POC [8]. When these methods are applied to mixtures covering a wide boiling point range not all of the individual components are well resolved. These techniques are referred to here as low-resolution gas chromatography (LRGC). LRGC has been used to characterize Norway spruce extractives in wood and process streams [8,9]. With LRGC, quantitation may be more appropriately performed by component class rather than for single components [8,10].

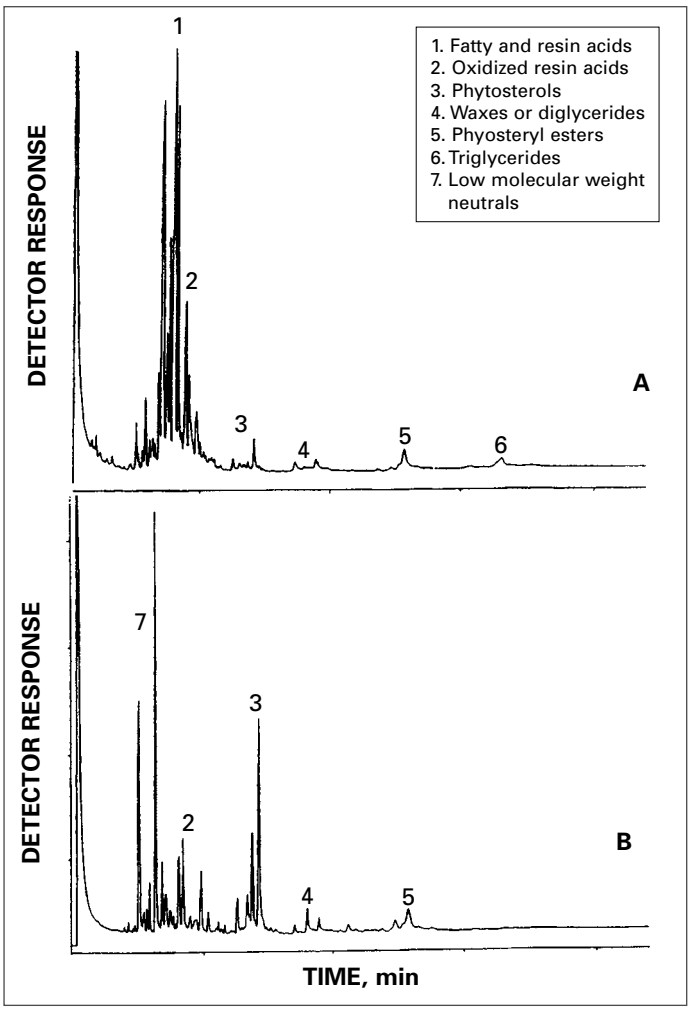
Analysis of TMP streams

Voss and Rapsomatiotis used methyl *tert*-butyl ether (MTBE) to extract resin and fatty acids from pulp-mill effluent [11]. Orsa and Holmbom [8] used MTBE to extract wood resin and lignans from TMP process streams and LRGC to characterize the extracts rapidly. Sithole *et al.* [10] used LRGC to characterize the acetone extracts of aspen wood and bark. In this study, we used acetone to extract wood meal prepared from western hemlock and lodgepole pine chips. Acetone was chosen because it solvates a wide range of extractives including native wood resin, lignans and oxidized resin acids.

When attempting to use LRGC to characterize lodgepole pine acetone extracts in a single chromatogram, oxidized resin acids and lignans partially coeluted with the lipophilic extractives. For this reason polar and nonpolar fractions were prepared from the acetone extracts and then analyzed separately. Depending upon the species, the nonpolar fractions included fatty acids, resin acids, phytosterols, waxes, diglycerides, phytosteryl esters, triglycerides, oxidized resin acids, and a variety of unidentified low molecular weight neutral compounds. The polar fractions of acetone extracts included flavonoids, lignans, stilbenes, oxidized resin acids, and low molecular weight carbohydrate-like components.



1. Methods summary for analysis of acetone extractives in wood chips.



2. LRGC of total nonpolar extractives in; A. Lodgepole pine, and B. Western Hemlock.

In this study, we found that the nonpolar extractives in acetone extracts of western hemlock could be quantitatively isolated from the total extract using hexane; however, complete recovery of the resin acids from lodgepole pine acetone extracts required a 5:1 blend of hexane:chloroform. We examined the LRGC and HRGC chromatograms to assess the effectiveness of this fractionation approach. Of the lipid component classes, only oxidized resin acids appeared in both the polar and nonpolar fractions. We further separated the nonpolar extractives into acid and neutral fractions using solid phase extraction (SPE). Chen *et al.* [12] originally demonstrated the use of SPE for separating wood resin into major lipid classes [12,13]. SPE was used here, however, only to the separate the acids from the neutral lipids. Polar fractions were analyzed by LRGC and HRGC without further fractionation.

Western hemlock extractives

Goldschmidt and Hergert [14] reported 0.237% ether soluble extractives in western hemlock sapwood; Hillis [15] reported 0.3%-1.3% ether soluble extractives in whole wood. Significant proportions of these extracts, however, were shown to be lignans, [14, 16]. Lipids actually comprise only a relatively small percentage of western hemlock extractives, with only 0.12% nonphenolic extractives reported from sapwood [16]. Studies have reported resin acids in hemlock [17,18] but these were not identified in conjunction with chromatography.

Hemlock flavonoids are relatively polar and are usually extracted with methanol. With exposure to air or light, flavonoids in fresh hemlock wood may polymerize to form insoluble tannin-like material [19, 20]. The acetone extractable polyphenols examined here in hemlock TMP-furnish were mostly lignans, and have been identified elsewhere. They include cedrusin, metairesinol, hydroxymetairesinol, allohydroxymetairesinol, oxometairesinol, conidendron, liovil, and pinoresinol [21]. Lignans also contribute to the discoloration of western hemlock lumber [21,22].

Lodgepole pine extractives

Fresh lodgepole pine contains 2.0%-3.4% nonvolatile lipophilic extractives, including fatty acids, resin acids, and other acids, as well as neutral diterpenes, phytosterols, waxes, diglycerides, phytosteryl esters, and triglycerides [23-25]. Differences exist between the extractives content of heartwood and sapwood, including a higher concentration of resin acids in heartwood. Ether extracts of the whole wood consist of 35% resin acids, 4% free fatty acids, 26% esterified fatty acids, 20% "other" acids, 5% phytosterols, and 10% neutral diterpenes. All of the eight common abietane and pimarane resin acids occur in lodgepole pine [24]. One study found all eight resin acids, but did not resolve palustric and levopimaric acid in their chromatograms [25]. Another group did not find levopimaric acid, but reported a large amount of palustric acid, possibly indicating these two were not resolved [23].

COMPONENT CLASS	CALIBRATION STANDARD	CCRRF
Fatty and resin acids	oleic acid	1.0
Oxidized resin acids	oleic acid	1.0
Phytosterols	stigmasterol	1.1
Waxes/diglycerides	di-stearin	0.7
Phytosteryl esters	cholesterol stearate	0.6
Triglycerides	tri-olein	0.5

I. Component class relative response factors (CCRRFs) used for LRGC analysis of nonpolar extractives.

SAMPLE	% NON-POLAR	% POLAR	% TOTAL
Lodgepole #1	2.08	0.50	2.58
Lodgepole #2	2.00	0.52	2.52
Average:	**2.04**	**0.51**	**2.55**
Hemlock #1	0.27	0.60	0.87
Hemlock #2	0.23	0.59	0.82
Average:	**0.25**	**0.60**	**0.85**

Table II. Polar and nonpolar extractives content of replicate chip samples by dry weight.

SAMPLE	FATTY/RESIN ACIDS	OXIDIZED RESIN ACIDS	PHYTO-STEROLS	WAXES/ DIGLY.	STERYL ESTERS	TRIGLY-CERIDES	OTHER NEUTRALS	TOTAL NEUTRALS
LRGC only*								
Lodgepole	63	17	2.9	2.8	7.7	6.3	na	20
Hemlock	29	14†	33	11	12	1.6	na	58
SPE/LRGC								
Lodgepole	55	14	2.8	2.9	7.6	6.3	11	31
Hemlock	18	12†	33	11	13	2.0	11	70

* Fatty/resin acid content overestimated due to inclusion of neutral components.
† In hemlock these were unidentified components

III. Comparison of percentages of nonpolar component classes in chip samples using LRGC and SPE/LRGC.

REPLICATE #	1	2	3	4	AVG.	ST DEV
Extract wt. (mg)	18.8	19.0	18.0	18.8	na	na
Acid fraction %	50.5	52.6	52.8	52.7	52.2	1.10
Neutral fraction %	48.4	47.9	47.2	48.4	48.0	0.57
% recovery	98.9	100.5	100.0	101.1	100.1	0.93

IV. SPE recovery and repeatability

Lodgepole pine heartwood also contains polyphenolic extractives, including flavonoids (pinocembrin and pinobanksin) and stilbenes (pinosylvan and pinosylvan monomethyl ether) [26]. Studies also described lignans, such as pinoresinol, in pine species [15]. Some of the characteristic polyphenols in pines, including pinobanksin, pinocembrin, and pinosylvan, lack hydroxylation on one aromatic ring and are therefore relatively lipophilic.

Oxidized resin acids

Abietane resin acids readily oxidize with exposure to oxygen, forming dehydroabietic acid and a variety of other oxidized resin acids with aging [27-29]. Abietane-type resin acids also oxidize during oxidative TMP bleaching [30]. Oxidized resin acids have not been reported in fresh lodgepole pine, but have been identified in individual diseased trees [31].

Following elution of fatty and resin acids in the LRGC chromatograms of lodgepole pine nonpolar extracts, we noted a range of unidentified peaks. We subsequently identified these peaks as oxidized resin acids using HRGC with MS detection and confirmed some using oxidized resin acid standards. When present, oxidized resin acids occurred more significantly in the polar fraction of lodgepole pine acetone extracts, and their content increased considerably with aging of the wood meal. We also oxidized reference resin acid compounds and examined the products using GCMS. Although not all of the oxidation products were fully characterized, this procedure aided identification of oxidized resin acids in the extracts because relative retention times and mass spectra of some chromatographic peaks could be directly compared.

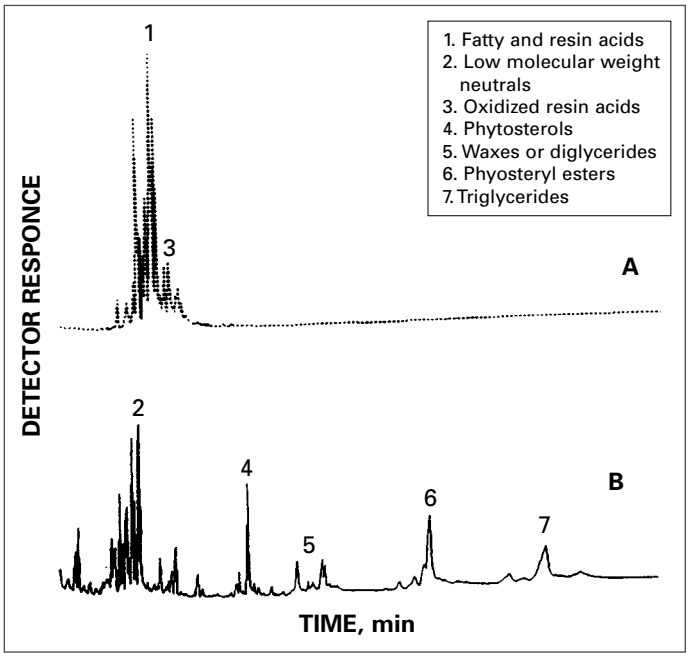
EXPERIMENTAL

Sample preparation

For this study, we obtained wood chips from a TMP mill in the northwestern United States. The chips came from the chip washing stage of TMP manufacture. We do not know the age of the wood at the time of collection. TMP made from this furnish was also obtained on the same day from various manufacturing stages at appropriate time intervals; the extractives in the TMP, as well as wash water, were also analyzed using the same approach [32]. The chips, still wet following collection, were air-dried overnight at room temperature to allow proper milling to produce wood meal for extraction. The chips were milled to 1 mm using a Wiley mill. The wood meal was then lyophilized and stored at –24°C in sealed containers if not extracted immediately. We allowed some of the wood meal to stand at room temperature for two months to examine changes in the extractives content over that time interval. The extractives content is reported on the weight basis of lyophilized wood meal.

Four grams of wood meal was Soxhlet extracted with 200 mL acetone for 8 h at 10 cycles/hour. We added 2 mL of an internal standard solution, containing pentadecanoic acid (0.25 mg/ml) in chloroform to the wood meal immediately before extraction. Soxhlet extraction for 10 h and 12 h did not increase the extractives yield. **Figure 1** shows the analytical scheme. Following extraction, the acetone was quickly removed by rotary evaporation at 45°C and the extracts were quantitatively transferred to tared aluminum weighing pans and rapidly dried to constant weight at room temperature under dry nitrogen.

The extracts were partitioned into polar and nonpolar fractions by recovering the nonpolar fraction using three 10 mL aliquots of hexane (for hemlock extracts) or three aliquots of 5:1 hexane/chloroform (lodgepole pine extracts). We dried the polar and nonpolar fractions under nitrogen, and weighed them again. We verified the added



3. LRGC of nonpolar extractives in Lodgepole pine following solid phase extraction; A. acid fraction, and B. neutral fraction.

weights of the two fractions against the initial weight of the total extract as a check. In addition, we compared LRGC and HRGC chromatograms of the polar and nonpolar fractions to ensure that the fractionation scheme was effective.

Fractions obtained using these methods typically weighed between 20-100 mg. We also processed method blanks through all the extraction and preparation steps. The method blanks weighed less than 0.3 mg and produced clean chromatograms. Both the polar and nonpolar fractions were completely soluble in pyridine, allowing for reliable derivatization and GC analysis. For silylation, approximately five mg of extractives was dissolved in 400 µL of pyridine in a GC autosampler vial and 100 µL of BSTFA + 10% TMCS was added. We heated the vials to 65ºC for 1 h and analyzed them within 24 h. Apparent degradation of the silyl derivatives was noted after 48 hours at room temperature. The samples could be stored in a desiccator at -20°C for many months, however, without noticeable changes in the chromatograms.

Low resolution GC

For LRGC analysis, we used a Perkin-Elmer Autosystem gas chromatograph equipped with programmable on-column injection port and a wide bore capillary column (J&W DB-1, 7.5 m x 0.53 mm, 0.15 µm film thickness). We used helium as the carrier gas and detection was by flame ionization detector (FID). The oven program was as follows: 110° to 280°C at 25°C/min, 280° to 310°C at 3°C/min, and a 3 min hold at 310°C. The injection port was kept 10°C above the column temperature throughout, and the detector was held at 325°C. We used an autosampler with a 0.2 µL injection volume.

The LRGC method was calibrated to report nonpolar extractives as percentages in six lipid component classes. Calibration was based on the averaged component class relative response factors (CCRRFs) derived from duplicate runs of a calibration standard containing a representative compound from five lipid component classes (**Table I**).

PEAK #	RET. TIME	ID	COMPONENT CLASS
1	13.65	Pentadecanoic acid (I.S.)	FA
2	16.47	Palmitic acid	FA
3	18.45	Heptadecanoic acid	FA
4	20.50	Linolenic acid	FA
5	21.07	Linoleic acid	FA
6	21.24	Oleic acid	FA
7	21.97	Stearic acid	FA
8	23.55	Pimaric acid	RA
9	24.00	Sandaracopimaric acid	RA
10	24.37	Isopimaric acid	RA
11	25.00	Palustric acid	RA
12	25.55	Levopimaric acid	RA
13	25.90	Dehydroabietic acid	RA
14	26.54	Abietic acid	RA
15	28.97	Neoabietic acid	RA
16	29.12	7-OH dehydroabietic	OXRA
17	29.59	Pinocembrin	FLAV
18	29.92	7-keto dehydroabietic	OXRA
19	30.47	Unidentified ox. resin acid	OXRA

V. Lodgepole pine nonpolar acid fraction obtained by SPE, identified using GCMS: (FA: fatty acid, RA: resin acid, OXRA: oxidized resin acid, FLAV: flavonoid).

Analysis of various lipid standards—including fatty acids, resin acids, oxidized resin acids, and phytosterols—yielded similar response factors for all these lipids, which eluted within 8 min. Decreased response was observed for higher molecular weight lipids, particularly polyunsaturated triglycerides. Because dehydroabietic acid and 7-hydroxy-dehydroabietic acid yielded similar response factors as oleic acid, we used oleic acid for calibration of fatty acids, resin acids, and oxidized resin acids. Because fatty and resin acids co-eluted to some extent by LRGC, we calibrated them as a single component class. The percentage of each component class (CC) comprising the nonpolar extracts was calculated using eq 1.

$$CC\ \% = [(CC\ area \div CCRRF)/\Sigma(CC\ area \div CCRRF)] \times 100\% \quad (1)$$

The percentage of each component class in the wood could be calculated by multiplying each CC% by the extract weight and dividing by the wood meal sample weight.

Depending upon the wood species, polar extracts included lignans, flavonoids, stilbenes, and oxidized resin acids. In addition, we tentatively identified a variety of low molecular weight compounds as carbohydrates based on characteristic TMS fragmentation patterns using GCMS. We did not attempt LRGC quantitation of the polar extracts, but did visually inspect the chromatograms to provide a general idea of the relative molecular weight of the component classes comprising those fractions. For example, the polar fractions of hemlock contained mostly lignans. LRGC analysis of the polar fractions also aided with verification of the polar/nonpolar fractionation step.

Solid phase extraction

We further separated the nonpolar extractives into acid and neutral fractions using an aminopropyl phase SPE cartridge (Alltech, 300 mg). We pretreated the cartridges with 3 mL hexane and loaded them with 15-20 mg of wood resin dissolved in 1 mL chloroform. The neutral fractions were eluted with 8:1 hexane:ether (2 x 2 mL) and the acid fractions were eluted with 98:2 ether:acetic acid (2 x 2 mL). LRGC and HRGC

confirmed the completeness of SPE separation. For routine sample processing, we only analyzed the acid fraction by HRGC. Compounds were identified on the basis of relative retention times vs. the internal standard. We did not attempt quantitation of specific acids here, but instead weighed the neutral anf acid fractions.

If we did not use SPE before LRGC analysis, then co-eluting neutral compounds caused overestimation of the fatty and resin acid content of lodgepole pine nonpolar extracts of about 10%. These low molecular weight neutral compounds may be hydrocarbons, resin alcohols, and resin aldehydes [24]. SPE effectively separated these low molecular weight neutral components from the acids, as verified by HRGC.

High resolution GC

We used a Perkin-Elmer Autosystem gas chromatograph equipped with a narrow-bore capillary column (J&W DB-5, 30 m, 0.25 mm diameter, 0.25 mm film) for the HRGC analysis. We used the following oven program: 155°C for 1 min upon injection, 3°C/min up to 300°C, ending with a 10 min hold at 300°C. The injection port temperature was 260°C, and the detector temperature was 310° C. Split injection (2.0 µL) was used with a split flow of 50 mLs/min. Detection was by FID, or electron impact mass spectrometry (EI-MS) at 70 eV.

Oxidized resin acids

We identified an LRGC elution time range for oxidized resin acids by analyzing oxidized resin acid standards, including 7-oxo and 7-hydroxy dehydroabietic acid, and by analysis of samples containing oxidized resin acids including wood rosin, aged lodgepole pine wood meal, and the products of an oxidation experiment. We analyzed the samples using both LRGC and HRGC with MS detection. Abietic acid and dehydroabietic acid were subjected to peroxide oxidization and many of the degradation product peaks matched relative retention times and mass spectra of peaks seen in samples. Lodgepole pine wood meal allowed to stand at room temperature for two months was reanalyzed to confirm the presence and identification of oxidized resin acids. Oxidized resin acids appeared in both the polar and non-polar fractions, but more abundantly in polar fractions.

RESULTS AND DISCUSSION

Extraction methods

Initial experiments indicated that acetone extraction provided higher recovery of wood resin components, oxidized resin acids, and lignans from wood meal than did sequential extraction with hexane followed by methylene chloride. The acetone extracts, however, required further partitioning into polar and nonpolar fractions before LRGC. When using acetone it was important to lyophilize the samples first in order to exclude water that would otherwise change the polarity of the extraction solvent. This caused extraction of tannin-like material that could not be analyzed by GC. In order to accurately determine the extract weights and ensure pyridine solubility for GC analysis, the fractions were best evaporated to dryness under nitrogen. Excessive exposure to air or heat cause insoluble precipitates to form, especially in nonpolar fractions. Provided the extracts were fully soluble in pyridine, the performance of the LRGC column was stable over many months, allowing analysis of hundreds of samples. This also served to keep the on-column injection system contaminant free.

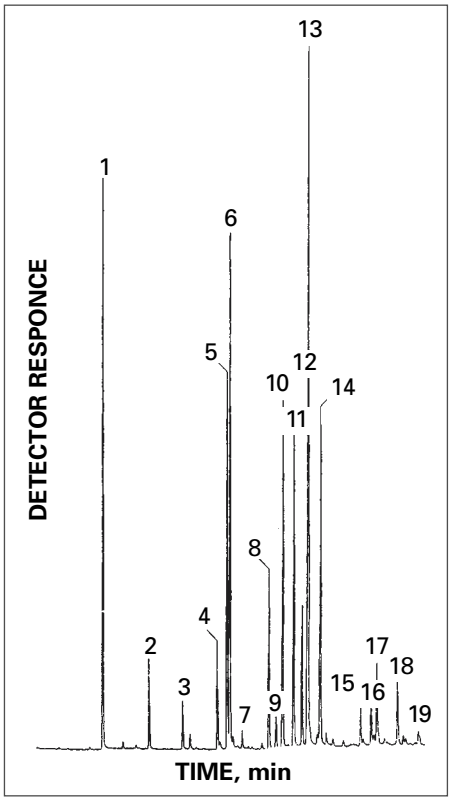
Total extractives

Lodgepole pine had significantly more acetone extractives than western hemlock, including about 10 times more nonpolar extractives (**Table II**). The polar extractives content of the two furnishes was similar; however, their individual composition was significantly different.

Nonpolar fractions by LRGC

The nonpolar extractives in lodgepole pine included compounds in eight lipid component classes: fatty acids, resin acids, oxidized resin acids, phytosterols, waxes and/or diglycerides, phytosteryl esters, triglycerides, and low molecular weight neutrals. Without SPE, the combined acids apparently accounted for almost 80% of the total lipophilic extract using LRGC (**Fig. 2a**). Using SPE followed by LRGC, the nonpolar extracts were actually comprised of 55% fatty and resin acids, and 14% oxidized resin acids. The difference between LRGC and SPE/LRGC results (11%) may reflect the content of neutral diterpenes (**Fig. 3, Table III**.).

The combined lipophilic acid content of lodgepole pine furnish (69%) was about 10% more than that reported elsewhere for fresh lodgepole pine [24, 25]. One study [23] indicated significantly more resin acids in lodgepole pine heartwood than in the sapwood, with heartwood extracts containing 55% free fatty and resin acids. Oxidized resin acids were not specifically reported in the studies cited above, but probably comprised part of the "other acids" reported [24, 25].



4. HRGC-MS total ion chromatogram of nonpolar acids in Lodgepole pine extracts (labeled as in Table V.).

Unidentified low molecular weight neutral components dominated the nonpolar extracts of western hemlock. This fraction also contained phytosterols, waxes or diglycerides, phytosteryl esters, and a small amount of triglycerides (**Fig. 2b**).

Solid phase extraction

To assess SPE recovery and repeatability, we separated four aliquots of lodgepole pine nonpolar extractives into acid and neutral fractions (**Table IV**).

Nonpolar acids HRGC analysis

Most of the hemlock nonpolar extracts were low molecular weight neutral compounds. Small amounts of fatty acids, including oleic acid and linoleic acid, were also present. In contrast, the nonpolar extracts of lodgepole pine were composed of almost 70% combined fatty

acids, resin acids, and oxidized resin acids. We observed all of the previously described fatty and resin acids in lodgepole pine nonpolar acid fractions (**Fig. 4; Table V**). We also identified a number of oxidized resin acids, and the flavonoid pinocembrin, in this fraction.

Resin acids in the lodgepole pine extracts were present in the abietane/dehydroabietic/pimarane ratio of 1.65/1.26/1.00. These are similar ratios to those reported for fresh lodgepole pine [24].

Polar fractions

The polar extractives in lodgepole pine included lignans, stilbenes, flavonoids, oxidized resin acids, low molecular weight carbohydrate-like compounds, and a small amount of unidentified high molecular weight material. Western hemlock extracts were comprised mostly of lignans, plus a small fraction of low molecular weight carbohydrate-like material.

Oxidized resin acid

In lodgepole pine wood meal aged for 2 months at room temperature, the ratio of abietane/dehydroabietic/pimarane resin acids changed from 1.65/1.26/1.00 to 1.22/2.10/1.00. We also identified mono- and di-hydroxy oxidized resin acids in these extracts. Many of the oxidized resin acids present in aged material were not apparent in original lodgepole pine furnish extracts.

CONCLUSIONS

Initial experiments indicated that acetone extraction of wood meal provided higher recovery of wood resin, lignans, and oxidized resin acids than did sequential extraction of wood meal with hexane and methylene chloride. To improve quantitation using LRGC, however, the acetone extracts may first need to be partitioned into polar and nonpolar fractions. Different solvent systems may work best to partition polar and nonpolar fractions from various wood species. For example, a 5:1 hexane:chloroform blend provided more reliable recovery of resin acids from lodgepole pine acetone extracts than did 100% hexane.

Partitioning the acetone extracts into polar and nonpolar fractions simplifies the LRGC chromatograms, allowing the nonpolar extract to be profiled without interference. However, ion exchange must be used to separate acids from neutrals. Otherwise, overestimation of fatty and resin acids may result due to co-elution of low molecular weight neutral compounds. SPE is a quick and simple way to accomplish this fractionation.

Using LRGC and HRGC together was effective for describing the composition of acetone extractives from Western hemlock and lodgepole pine TMP furnish. LRGC was used to profile both polar and nonpolar fractions, thus allowing for quantitative and semi-quantitative interpretation of many extractives classes. We also used HRGC qualitatively and quantitatively to analyze a range of individual components. Use of an internal standard simplifies peak identification and makes quantitation of individual components possible. We found various oxidized resin acids in the lodgepole pine extracts, allowing for a method to determine chip aging effects. **TJ**

ACKNOWLEDGEMENTS

Larry LaFleur from NCASI, Corvallis, Oregon, provided resin acid standards and consultation. William McKean at the University of Washington College of Forest Resources also provided valuable consultation.

LITERATURE CITED

1. Grob, K., *On-Column Injection in Capillary Gas Chromatography: Basic Technique, Retention Gaps, Solvent Effects*, Alfred Huethig Verlag, Heidelberg, Germany, (1987).
2. Geeraert, E., and Sandra, P., *J. High Res. Chrom. and Chrom. Comm.* 8: 415-422(1985).
3. Hinshaw J.V. Jr., and Seferovic W., 9(2): 69-72 (1986).
4. Lercker G., *J. Chromat.* 279: 543(1983).
5. Mares, P., *Prog. Lipid R.* 27(2), 107-133(1988).
6. Chapman, R., Nugent, H., and Bolker, H., "An improved method for the analysis of wood extractives and its application to Jack pine (*Pinus banksiana Lamb.*)," Transcript, Technical Section, Canadian Pulp and Paper Association (CPPA), Montral, Quebec, Canada, 1(4): 113-122(1975).
7. Nugent, H., Allen, L., and Bolker H.I., "Effect of seasoning of the acetone extractives composition of the wood from black spruce, Jack pine and trembling aspen," Transcript, Technical Section, CPPA, TR 103-109(1977).
8. Orsa, F., and Holmbom, B., *J. Pulp Pap. Sci.* 20(12): 361(1994).
9. Orsa, F., Holmbom, B. and Thornton, J., *Wood Sci. Technol.* 31(4): 279(1997).
10. Sithole, B.B., Sullivan, J.L. and Allen L.H., *Holzforschung* 46(5): 409(1992).
11. Voss, R. H. and Rapsomiotis, A., *J. Chromat.* 346: 205(1985).
12. Chen, T., Breuil, C., Carriere S., and Hatton, J. V., *Tappi J.* 77(3): 235(1994).
13. Kaluzny, M.A, Dunca, L.M., and Merritt, M. V., *J. Lipid Res.* 26, 135-140(1985).
14. Goldschmid, O., Hergert,H. L., *Tappi J.* 44(12): 858-870(1961).
15. Hillis, W.E., "The distribution and formation of polyphenols within the tree", *in* Wood Extractives, W.E. Hillis Ed., Academic Press, New York, Chapter 2: 59-131(1962).
16. Barton, G.M., *Wood Fiber* 2(2): 144(1970).
17. Polcin, J. and Rapson W.H., *Pulp Pap. Mag. Can.* 72(10): (T324) 84-90(1971).
18. Polcin, J., Wayman, M., Anderson, C. B., and Rapson, W.H., *Pulp Pap. Mag. Can.*, 70(11): (T410)91(1969).
19. Hergert, H.L., *Forest Prod. J.* 10(11): 610(1960).
20. Hrutfiord, B.F., Luthi, R., and Hanover, K.F., *J. Wood Chem. Technol.* 5(4): 451(1985).
21. Kawamura, F., Ohashi, H., Jawai, S., Teratani, F., and Kai, Y., *Mokuzai Gakkaishi* 42(3): 293(1996).
22. Kawamura, F., Ohashi, H., Jawai, S., Teratani, F., and Kai, Y., *Mokuzai Gakkaishi* 42(3): 301(1996).
23. Gao, Y., Chen, T. and Breuil C., *Holzforschung* 49(1): 20 (1995).
24. Conner, A.H., Diehl, M.A. and Rowe, J.W., *Wood Science* 12(3): 183(1980).
25. Anderson, A.B., Riffer, R., and Wong, A., *Phytochemistry* 8(10): 2401-2403 (1969).
26. Lowman, A. A., "The effect of heartwood fungi of *Pinus contorta* var. *latifolia* on pinosylvin, pinosylvinmonomethyl ether, pinobanksin, and pinocembrin", Can. J. Bot. 48(4): 737(1970).
27. Hemingway, R.W., Nelson, P.J., and Hillis, W.E, *Tappi* 54(1): 95(1971).
28. Minor, J.C., Schuller, W.H., and Lawrence, R.V., *Tappi* 48: 9, 541-542,(1965).

29. Lawrence, R. V., *Tappi* 42(10): 867(1959).
30. Ekman, R. and Holmbom, B., *Nord. Pulp Pap. Res. J.* 4(1): 16(1989).
31. Ayer, W.A. and Migaj, B.S., *Can. J. Bot.* 67: 1426(1989).
32. Hanneman, A. "Modification of wood extractives and hemicelluloses during thermomechanical pulping: implications for newsprint sizing," University of Washington Doctoral Dissertation, Seattle, WA, (1999).

Received: January 15, 2001
Revised: October 29, 2001
Accepted: November 11, 2001

This paper is also published on TAPPI's web site www.tappi.org and summarized in the September *Solutions! for People, Processes and Paper* magazine (Vol. 85 No. 9)

INSIGHTS FROM THE AUTHORS

Reliable analytical methods are needed to investigate the behavior of various wood extractives during TMP pulping and newsprint manufacture. They must provide results about extractives classes and about specific components. The gas chromatographic (GC) methods we used can be developed relatively quickly and inexpensively and can provide detailed information about wood extractives content and composition in many types of sample matrices.

The research rationale and general method development issues were similar to those used by others to analyze extractives in Norway spruce and TMP. We modified the methods significantly and adapted them to two other types of TMP furnish having widely differing extractives composition. We also tried to improve on the reporting of polar extractives, including oxidized resin acids, and to simplify the interpretation of chromatograms by pre-GC fractionation. This significantly improved quantification. Using this approach, detailed information about component classes and the individual components of interest was possible.

The methods for furnish analysis we started with were originally developed to target a variety of TMP cost and quality issues, so we needed detailed information about a wide range of wood extractives. The development of methods suitable for use with a variety of furnish types and sample matrices was the most difficult goal of this research. Specific application issues included wash water treatment and TMP self-sizing.

Extractives have effects on many aspects of TMP and newsprint production that are often disproportionate to the extractives content in wood. Production decisions could benefit significantly from having reliable detailed knowledge about extractives content and composition at various stages of production. This type of information can be developed readily and inexpensively. Conventional wisdom about self-sizing and other aspects of extractives behavior may need to be modified to accommodate new information obtained from operating mills.

A relatively low cost analytical chemistry lab equipped to run these methods quantitatively (in conjunction with data quality control) could potentially produce useful information regarding free and metal-bound extractives at all points of TMP and newsprint manufacture. This would potentially lead to new deresination methods, new wastewater treatment strategies, reduced chemical usage, and improved ways to use natural wood resin for TMP sizing. These programs require reliable and detailed data about extractives content in various sample types.

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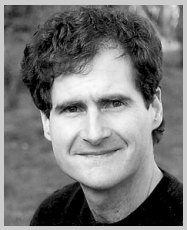
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