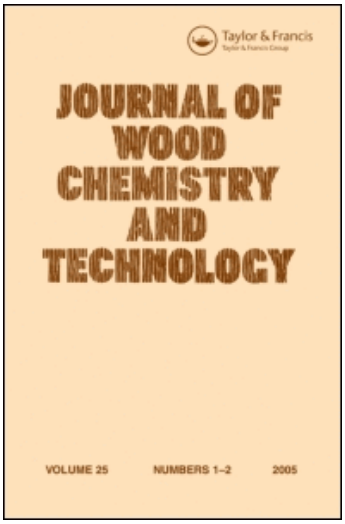

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Summative Analysis of Nine Common North American Woods

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SUMMATIVE ANALYSIS OF NINE COMMON NORTH AMERICAN WOODS

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ABSTRACT

The summative analysis of lignocellulosic materials has heretofore been a complicated process or the analysis has been incomplete. The Bomb/HPLC summative analysis method presented in this report results in a complete analysis of woody materials using a sample preparation scheme that is easily adopted into a normal laboratory routine. The method relies on HPLC for the majority of the component analyses. To demonstrate the applicability and reproducibility of the Bomb/HPLC method, ten wood samples, from nine different wood species, were analyzed in triplicate and the summative analysis of each sample was effected. The ten woods analyzed were: American beech *(Fagus grandifolia)*, Quaking aspen *(Populus tremuloides)*, Black cherry *(Prunus serotina)*, Sugar (Hard) maple *(Acer saccharum)*, Red (Soft) maple *(Acer rubrum)*, White ash *(Fraxinus americana)*, Yellow birch *(Betula verrucosa)*, Douglas fir heartwood and Douglas fir sapwood *(Pseudotsuga menziesii)*, and White fir sapwood *(Abies concolor)*. The average summative analysis for the group of thirty samples was 99.13 ± 0.51% on an unextracted basis, 99.07 ± 0.45% on an extractive-free basis. There were no significant unidentified peaks in any of the HPLC chromatograms. The range of mass balance determinations for the group of ten wood specimens on unextracted and extractive-free bases was 98.43 to 99.63% and 98.31 to 99.60%, respectively.

INTRODUCTION

In the past, summative analysis schemes and methods have been unable to account for a total mass balance of a wood sample. Though analytical methods for wood analyses, such as those available from

TAPPI Standards[1] and other sources,[2-5] have been sufficient to account for most of the wood components, summative analyses using these methods have typically been deficient (or in excess) by about ten percent.[6] Thus, reports of wood summative analyses in the literature have usually been corrected via normalization.[7,8] While, by design, normalization assures a perfect summative analysis, the underlying assumption of its use is that all of the analytical techniques used were in error by the same factor. Hence, the fractions of the components of wood which are present in large quantities, such as glucose, are adjusted by a larger amount than components that are present in smaller quantities, such as the uronic acids, even though the glucose determination has been one of the most reliable and accurate and the uronic acid determination one of the most doubt-filled. Furthermore, normalizing completely ignores the possibility of undetected or unknown compounds in the wood sample. Time, which has brought improved analytical tools and methods, has resulted in improvement in wood analysis, but a summative analysis scheme that completely accounts for all of the wood material has remained elusive.

The objective of this summative analysis study was the development of a summative analysis scheme that could be easily implemented as routine, yet would provide a complete accounting of the starting material without normalization. In a previous paper, "The Complete Analysis of Wood Polysaccharides Using HPLC"[9], a comprehensive method for the analysis of the polysaccharide fraction of a wood sample, the Bomb/HPLC analysis method, was introduced and demonstrated to be reproducible. This method utilizes sealed vessels to contain the volatiles during hydrolysis and High-Performance Liquid Chromatography (HPLC) to effect the determination of the various polysaccharide moieties and their degradation products.

A second paper concerned with wood analysis, "Simplified Analysis of Acid Soluble Lignin"[10], introduced a novel method, the reKlasonation of Klason lignin, for the determination of absorptivities of acid soluble lignins (ASL). It was found that ASL is actually an acidic degradation product of Klason lignin. Thus,

the reKlasonation method involves repeated hydrolysis of known weights of Klason lignin to arrive at solutions of ASL of known concentration. By analyzing these solutions with ultraviolet (UV) spectroscopy at 205 nm, the absorptivity of an ASL can be calculated for use in determining the concentration of that ASL in a wood hydrolysate.

The final step in the development of the Bomb/HPLC summative analysis method was to demonstrate the reproducibility and applicability of the method as a whole over a range of different wood specimens. Thus, ten different woods from nine wood species were analyzed in triplicate, and the chemical analysis of each sample was determined. The ten woods analyzed were: American beech *(Fagus grandifolia)*, Quaking aspen *(Populus tremuloides)*, Black cherry *(Prunus serotina)*, Sugar (Hard) maple *(Acer saccharum)*, Red (Soft) maple *(Acer rubrum)*, White ash *(Fraxinus americana)*, Yellow birch *(Betula verrucosa)*, Douglas fir heartwood and Douglas fir sapwood *(Pseudotsuga menziesii)*, and White fir sapwood *(Abies concolor)*.

A flow-sheet for the Bomb/HPLC method is given in Figure 1. The discussions concerning the analytical procedures that are used in the method are presented, generally, in the order that they occur in the flow-sheet.

EXPERIMENTAL

Wood Preparation and Analyses

The same procedures were used for all of the wood specimens. A debarked bolt was first hammer-milled, then Wiley-milled to -40 mesh. The resulting comminuted wood was extracted, then analyzed for protein and ash. In addition, samples were utilized for extractives determinations.

Preparation of Extractive-free Comminuted Wood

Approximately 80 g (air dry) of each of the comminuted woods was extracted with a sequential series of 2:1 benzene:ethanol, 95% ethanol, and water. The resulting extractive-free wood samples were

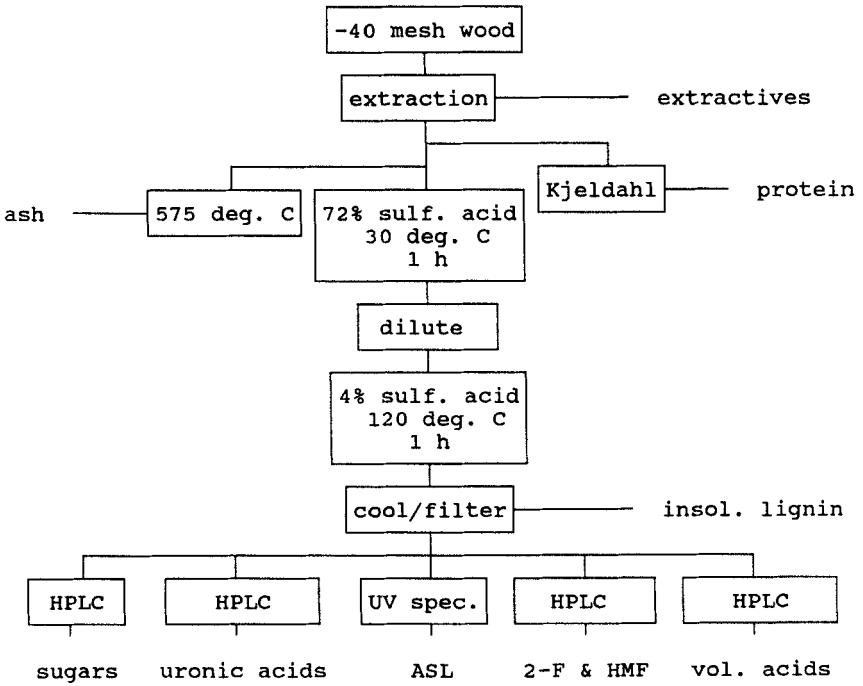

Figure 1. Flow-sheet for the Bomb/HPLC summative analysis method.

used for the summative analyses. The detailed preparative procedure was described previously.[9]

Extractive Content Determination

The extractive contents of the unextracted comminuted wood samples were analytically determined using basically the same conditions as in the "Extraction of Wood" preparative procedure, except the scale was considerably smaller. In determining the extractive contents, 1 g of oven-dried comminuted wood was Soxhlet extracted in a tared (0.0001 g) alundum extraction thimble, using 150 ml of solvent at each stage. The thimble containing the comminuted wood was freed of solvent with the aid of vacuum before each

solvent change. For the water extraction step, the Soxhlet extractor was also used with 150 ml of water. However, the condenser was not used for the first few minutes during the water extraction in order to distill any residual solvent. At the conclusion of the water extraction step, the thimble and its contents were again oven-dried to determine the total net weight loss. No effort was made to determine the weight loss after each intermediate stage. Therefore, only the total extractives contents are reported.

Protein Determination

The protein contents of the extracted woods were determined in duplicate according to TAPPI Standard T 418 om-85, "Organic Nitrogen in Paper and Paperboard".[1]

Ash Determination

The ash contents of the extracted woods were determined according to TAPPI Standard T 211 om-85[1], using 2 g samples (weighed ± 0.0001 g), in duplicate, in a muffle furnace at 575 ± 25 °C. Porcelain ashing crucibles were used.

Hydrolytic Method

The hydrolysis stage of the summative analysis method that has been developed was discussed in detail in a previous work.[9] The sample size for all of the wood specimens was approximately 0.35 g, determined to 0.0001 g.

Acid Insoluble Lignin

The mass of insolubilized lignin for each of the samples was obtained by filtering the cooled hydrolysate through tared medium-porosity sintered glass filter crucibles. The retained solids were washed and the oven-dried mass determined by drying in a laboratory oven at 105 °C.

Polysaccharide Analysis

The analysis of the polysaccharide moieties, including their degradation products, was effected using HPLC. The sample preparation procedures, equipment, representative chromatograms and calculation techniques have been presented in detail in a previous report.[9]

Acid Soluble Lignin

The acid solubilized lignin (ASL) fraction for each of the wood samples was determined by ultraviolet (UV) measurement at 205 nm of appropriate dilutions of the respective filtered hydrolysates. The ASL fraction was calculated using a modified Beer's law equation, given below. This equation was derived in a previous work.[10]

$$\%ASL = \frac{A * V - 19.14 * 250 * M_f}{a_L * S_w} * 100$$

where:

A = absorbance at 205 nm (assumes 1 cm pathlength)
V = theoretical total volume of UV solution (dilution factor times hydrolysate volume, in ml)
19.14 = 205-nm absorptivity of an equal mixture of 2-F and HMF (ml/mg-cm)
250 = volume of hydrolysate (ml)
M_f = concentration (mg/ml) of 2-furaldehyde (2-F) and 5-(hydroxymethyl)-2-furaldehyde (HMF) in hydrolysate (by HPLC)
a_L = absorptivity of ASL (ml/mg-cm)
S_w = sample weight of wood, in milligrams

The absorptivities for the ten woods were determined using the reKlasonation procedure that was introduced in "Simplified Analysis of Acid Soluble Lignin".[10] The procedure used for each wood was identical, and had been found to give ASL solutions whose absorbance at 205 nm was similar, with identical dilution, to the absorbance of a wood hydrolysate prepared by the standard method. Duplicate, 1 g samples of previously prepared Klason lignin, weighed to 0.0001 g, were hydrolyzed with 40 ml of premixed 4% sulfuric acid

solution at 103 kPa (120 °C) for 1 h in an autoclave. Once these reKlasonation solutions were cool, the remaining solids were determined in the normal manner. The hydrolysate for each sample was then analyzed for polysaccharide moieties and degradation products, as has been described previously[9], and the total amount of solubilized lignin determined by difference. The solution was then analyzed by UV spectroscopy and, using the maximum that occurred at approximately 205 nm, the absorptivity was calculated using Beer's law. It should be noted that, in the case of the softwood ASL analyses using UV spectroscopy, the amount of ASL present in the wood hydrolysates was small compared to the amount of HMF. As a result, the UV scans of the softwood hydrolysates more closely resemble a scan of HMF, rather than ASL (Figure 2). For this reason, the ASL contents of the softwood hydrolysates were calculated from the absorbance at exactly 205 nm. This approximation incurs negligible error in the determination.

RESULTS AND DISCUSSION

The results and calculated absorptivities from the reKlasonation experiments are given in Table 1.

In "Simplified Analysis of Acid Soluble Lignin"[10], it was found that the reKlasonation method for determining the absorptivity of ASL yields absorptivities that are approximately one half of the absorptivities that have been determined for ASL by researchers using other methods. The possible reasons for this discrepancy were discussed in detail. The values for the absorptivities for the ten woods, as determined in this study and reported in Table 1, are, with the exception of white fir, all less than 60 ml/mg-cm. In the case of white fir, the ASL determined was too low to permit calculation of an absorptivity that is not subject to appreciable error. However, for the other nine woods, the determinations of ASL involved a readily measurable, on the order of 10 mg, weight loss. Furthermore, the calculated absorptivities for duplicate samples were consistent. It is believed that the absorptivities for ASL, as calculated using the reKlasonation method, yield a true measure of the lignin solubilized in Klason-type acid hydrolysis procedures.

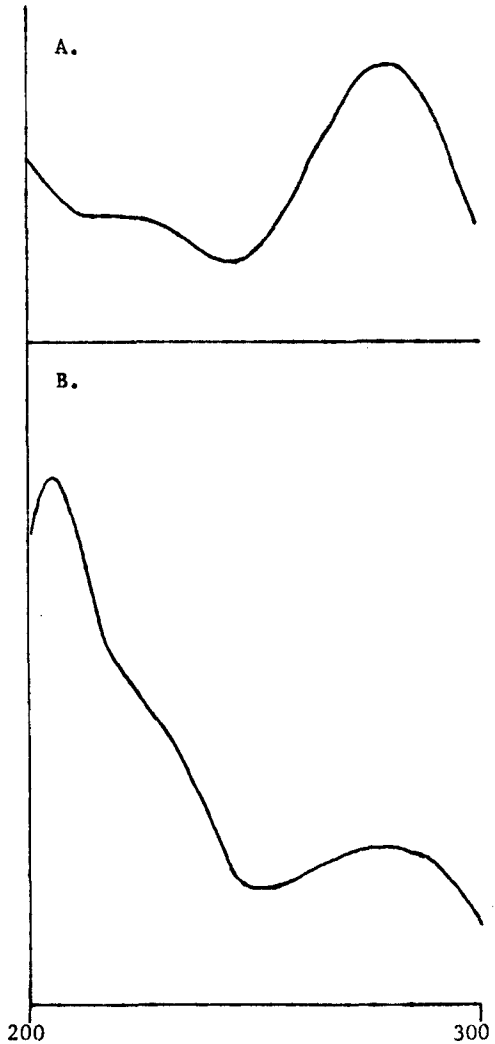

Figure 2. UV spectra of a softwood hydrolysate (A) and a reKlasonation hydrolysate from the same wood sample (B). Due to the small amount of ASL present in the wood hydrolysate, the spectrum of the wood hydrolysate more closely resembles the spectrum of HMF. The spectrum of the reKlasonation sample, while still exhibiting a high absorbance at 280 nm, more closely resembles an ASL spectrum. The UV spectrum of HMF was presented in an earlier report.[10]

TABLE 1
Results from the ReKlasonation of the Ten Wood Lignins

	solubles (mg)	2-F (mg)	HMF (mg)	xylan (mg)	glucan (mg)	GUAX (mg)	GUA (mg)	ASL (mg)	a (ml/mg-cm)	a^{avg} (ml/mg-cm)
AB-1	9.0	---	---	---	---	---	---	9.0	55.9	55.0
AB-2	9.5	---	---	---	---	---	---	9.5	54.0	
AS-1	17.0	0.08	---	0.53	1.90	0.22	0.14	14.1	45.4	45.8
AS-2	15.0	0.06	---	0.48	2.43	0.03	0.07	11.8	46.2	
BC-1	16.0	0.11	---	0.58	0.55	0.20	---	14.6	56.9	56.0
BC-2	16.1	0.08	---	0.53	0.53	0.16	---	14.8	55.1	
HM-1	13.8	---	---	0.52	0.47	---	---	12.8	48.6	48.5
HM-2	13.4	---	---	0.58	0.48	---	---	12.3	48.4	
SM-1	16.5	0.08	---	0.65	0.34	0.44	---	14.6	54.2	56.7
SM-2	15.0	0.04	---	0.64	0.36	0.26	---	13.7	59.2	
WA-1	17.0	0.08	---	0.74	0.44	0.63	---	15.1	51.0	49.7
WA-2	20.3	0.07	---	0.68	0.39	0.38	---	16.8	48.5	
YB-1	12.4	0.06	---	0.56	0.47	0.56	---	10.8	46.7	48.3
YB-2	11.7	0.08	0.03	0.44	0.44	0.25	---	10.5	49.8	
DFH-1	3.8	---	---	---	0.61	0.06	---	3.1	32.0	32.1
DFH-2	4.4	---	---	---	0.50	0.04	---	2.9	32.2	
DFS-1	7.2	---	---	0.51	2.33	0.08	---	4.3	25.8	24.9
DFS-2	7.6	---	---	0.38	2.45	---	---	4.8	24.0	
WF-1	1.7	---	---	0.18	0.42	---	---	1.1	82.4	84.5
WF-2	1.6	---	---	0.32	0.12	0.06	---	1.1	86.5	

KEY: GUAX = 4-O-methyl-glucurono-xylose, GUA = 4-O-methyl-glucuronic acid (anhydro), --- = not present or too low to detect. Note: the beech lignin had been reKlasonized eight times prior to this experiment.

Results of the Analysis of Ten Woods

The average summative analyses, and the standard deviations, for the ten woods are reported in Table 2.

The only value for any of the woods that is not listed in the tables is the ASL absorptivity. The absorptivities have been previously listed in Table 1. It should be noted that the values in Table 2 are given for unextracted wood even though most of the analyses were performed on extractive-free wood. This was done to provide summative analyses for wood (unextracted) as it is used in chemical conversion processes. However, since, in the wood chemistry literature, comparisons of lignocellulosic materials are made using extractive-free wood, summary tables of the average summative analyses of the triplicate samples on an extractive-free basis are presented in Table 3.

The method used to calculate the whole wood values was to analyze the extractive-free woods and determine the extractive-free

TABLE 2
Average Summative Analyses (Unextracted Basis) for the Ten Woods

	Beech	Aspen	Cherry	H.Maple	S.Maple	W.Ash	Birch	D.Fir H	D.Fir S	W.Fir
glucan	40.58	45.24	39.13	40.49	39.94	39.65	38.06	40.27	42.95	44.09
xylan	16.32	15.03	17.82	15.30	15.80	18.17	14.63	4.40	3.93	4.80
arabinan	0.63	0.39	0.45	0.61	0.67	0.43	0.83	0.56	0.58	0.79
galactan	1.65	1.06	1.30	1.15	1.14	1.85	1.28	2.41	2.56	1.40
mannan	0.98	1.50	1.24	2.68	2.45	1.34	2.27	11.11	11.90	11.42
O-Me-GUA (1)	2.36	2.12	1.93	2.52	2.40	2.18	1.91	0.94	1.00	1.15
gluc acid(2)	0.12	0.13	0.14	0.15	0.19	0.09	0.11	0.08	0.00	0.08
gal acid (3)	1.30	0.56	0.51	0.53	0.34	0.81	0.62	0.11	0.09	0.48
lignin	26.16	21.42	25.56	27.49	26.19	25.66	26.96	27.66	28.62	29.42
acetyl	3.64	3.33	3.21	3.15	3.20	3.36	2.82	0.57	1.20	1.21
extractives	4.91	7.23	8.13	4.99	5.87	5.51	8.93	10.58	6.27	4.11
protein	0.12	0.08	0.10	0.10	0.13	0.27	0.10	0.16	0.18	0.12
ash	0.31	0.22	0.14	0.32	0.27	0.26	0.24	0.08	0.14	0.33
total	99.11	98.43	99.63	99.50	98.58	99.58	98.75	98.94	99.40	99.40

TABLE 2-SD
Standard Deviations for the Summative Analyses

	Beech	Aspen	Cherry	H.Maple	S.Maple	W.Ash	Birch	D.Fir H	D.Fir S	W.Fir
glucan	0.11	0.16	0.13	0.26	0.19	0.06	0.14	0.11	0.20	0.17
xylan	0.04	0.13	0.17	0.15	0.15	0.21	0.17	0.03	0.04	0.10
arabinan	0.01	0.02	0.03	0.02	0.03	0.01	0.04	0.01	0.02	0.02
galactan	0.03	0.06	0.05	0.01	0.04	0.05	0.04	0.18	0.09	0.02
mannan	0.03	0.05	0.02	0.07	0.02	0.02	0.18	0.14	0.13	0.20
O-Me-GUA (1)	0.07	0.08	0.11	0.04	0.07	0.06	0.04	0.15	0.06	0.05
gluc acid(2)	0.01	0.03	0.04	0.03	0.03	0.01	0.01	0.00	0.00	0.02
gal acid (3)	----	----	----	----	----	----	----	----	----	----
lignin	0.05	0.26	0.34	0.19	0.22	0.23	0.18	0.08	0.35	0.25
acetyl	0.02	0.04	0.06	0.03	0.07	0.08	0.09	0.10	0.02	0.01
total	0.12	0.31	0.23	0.27	0.36	0.57	0.12	0.56	0.16	0.52

(1) 4-O-methyl-glucuronic acid
(2) glucuronic acid
(3) galacturonic acid

TABLE 3
Average Extractive-free Summative Analyses for the Ten Woods

	Beech	Aspen	Cherry	H.Maple	S.Maple	W.Ash	Birch	D.Fir H	D.Fir S	W.Fir
glucan	42.68	48.77	42.59	42.62	42.43	41.96	41.79	45.03	45.82	45.98
xylan	17.16	16.33	19.40	16.10	16.79	19.23	16.06	4.92	4.19	5.01
arabinan	0.46	0.42	0.49	0.64	0.71	0.46	0.91	0.63	0.62	0.82
galactan	1.74	1.14	1.42	1.21	1.21	1.96	1.41	2.70	2.73	1.46
mannan	1.03	1.62	1.35	2.82	2.60	1.42	2.49	12.42	12.70	11.91
O-Me-GUA (1)	2.48	2.29	2.10	2.65	2.55	2.31	2.10	1.05	1.07	1.20
gluc acid(2)	0.13	0.14	0.15	0.16	0.20	0.10	0.12	0.09	0.00	0.08
gal acid (3)	1.37	0.60	0.56	0.56	0.36	0.86	0.68	0.12	0.10	0.50
lignin	27.51	23.09	27.82	28.93	27.82	27.16	29.60	30.93	30.53	30.68
acetyl	3.83	3.59	3.49	3.32	3.40	3.56	3.10	0.64	1.28	1.26
protein	0.13	0.09	0.11	0.11	0.14	0.29	0.11	0.18	0.19	0.13
ash	0.33	0.24	0.15	0.34	0.29	0.28	0.26	0.09	0.15	0.34
total	99.06	98.31	99.60	99.47	98.49	99.56	98.63	98.81	99.36	99.37

(1) 4-O-methyl-glucuronic acid
(2) glucuronic acid
(3) galacturonic acid

summative analyses. Then the percentages of the constituents that were determined in the extractive-free wood summative analyses were adjusted to an unextracted wood basis using the extractives content that was determined for each wood analyzed. The factor used to adjust each of the values in the summative analyses from an extractive-free wood basis to an unextracted wood basis is (100 - % extractives)/100.

The polysaccharide moieties are reported in Tables 2 and 3 as the anhydromonomer that would have existed in the wood. This calculation was made only for the constituents, and their degradation products, of the cellulose and hemicelluloses. In the case of ASL, protein, and other compounds, the method of analysis accounts the weight of the polymeric material as it occurs in the original wood. The factors used to determine the conversion from monomer to anhydromonomer have been reported previously.[9] The degradation products formed from hexose sugars, HMF and levulinic acid, are reported as glucan since it represents the majority of hexose in the wood. Similarly, the contribution due to 2-F is reported as xylan.

As shown in Tables 2 and 3, the Bomb/HPLC summative analysis method reproducibly accounted for essentially all of the ten woods analyzed. The average summative analysis for the group of thirty samples was 99.13 ± 0.51% on an unextracted basis, 99.07 ± 0.45% on an extractive-free basis. There were no significant unidentified peaks in any of the HPLC chromatograms. The range of mass balance determinations for the group of ten wood specimens on unextracted and extractive-free bases was 98.43 to 99.63% and 98.31 to 99.60%, respectively.

There are a number of factors that were undetermined in this study that might contribute to the Bomb/HPLC summative analysis. For example, the exact contribution of galacturonic acid in the wood specimens was not determined; this contribution might be greater than the estimates that were made in this study.

Methanol, formed from cleaved methoxyl groups, was another compound that was not ascertained. Methanol can be formed from the demethoxylation of 4-O-Me-glucuronic acid and lignin. When 4-O-Me-

glucuronic acid demethoxylates glucuronic acid is formed. However, very little glucuronic acid, on the order of 0.1%, was observed in the wood analyses and it was not necessarily derived from 4-O-Me-glucuronic acid. Thus, the contribution of uronic acid methoxyl, if any, is clearly small. Small amounts of lignin methoxyl, on the other hand, have been reported to be susceptible to cleavage under acidic conditions[11], and ,therefore, it is likely an undetermined contributor to the mass balance. An analysis of the hydrolysates by GC would be one means of determining the methanol content. Unfortunately, the acidity of the hydrolysates precludes the use of GC as an analytical tool in determining the methanol content of the solutions directly[12], though a preparation procedure could possibly be developed. The methanol concentration is too small to be determined by HPLC using RI detection. However, HPLC using PAD might be a possible analytical tool to be used in studying the existence of methanol in the Bomb/HPLC wood hydrolysates.

There is possibly another undetermined factor in the summative analysis scheme that involves the lignin. During the 72% sulfuric acid hydrolytic step in the Klason procedure, the lignin may lose water to condensation/dehydration reactions. The extent of this dehydration is unknown and difficult to determine since a method for the preparation of a true native (proto) lignin has yet to be devised. If proto-lignin could be prepared/isolated, the dehydration of the lignin during the Klason procedure could be quantified by the determination of the C-H-O balances of both the proto-lignin and the Klason lignin; the percentage of carbon in the Klason lignin would be higher than that of the proto-lignin due to the loss of water in the Klason lignin. However, for the method to be viable, the C-H-O balance of the Klason lignin would have to be corrected for the loss of methoxyl and residual polysaccharides during the hydrolysis. Clearly, the problems involved in the study of the dehydration of lignin during strong acid hydrolysis will not be easily resolved.

The analysis of lignin is not the only area where small fractions may have been overlooked or not detected. The HPLC method

used in the determination of the carbohydrates indicated that only glucose, xylose, arabinose, mannose and galactose were present in the wood hydrolysates. However, it has been reported in the literature that rhamnose and fucose are moieties in the hemicelluloses of at least some of the woods that were used in this study.[13] Whether these compounds were removed as extractives in the extraction procedure, or merely present in quantities that were too small to detect, is not known. It is conceivable that there could be several wood components included in the polysaccharide and/or lignin moieties that exist in such small quantities that they are not detected using the analytical methods that are described in this paper. Yet the combined mass of these compounds could account for the remaining small percentage of the extractive-free material balances. Unfortunately, in the chemical analysis of wood, it is difficult to determine whether chemical species that are observed during an analytical procedure are actual wood components or artifacts of the sample preparation. The presence of the glycolic acid in the "acids #2" preparations[9] is a good example of such a phenomenon. Thus, though the chromatograms would surely indicate more peaks, simply using larger volumes of hydrolysate or different methods in the HPLC sample preparations would not necessarily result in the elucidation of more wood components.

Finally, the determination of the moisture content of the air-dried extractive-free wood samples is an analysis that is potentially in error. The moisture content determination is one of the most critical procedures in any summative analysis method since the calculated moisture content is used to establish the theoretical "oven-dried" weights of the wood samples that are processed in the analytical procedures. The sample weight directly affects all of the other analyses and any error in its determination puts the summative analysis in error. It has been observed, by this investigator and others, that the removal of residual benzene and ethanol after an extraction procedure is difficult to achieve. Indeed, their removal cannot be effected by oven drying but instead require displacement by extraction with water.[12] Clearly, these

organic solvents become strongly bonded to wood moieties. If this is the case, then the precise determination of wood freed of bound water by oven-drying is even more difficult, since water has an even greater propensity to form strong bonds with wood, in this case hydrogen bonds, than the compounds noted. Thus, some residual water could remain bonded in the wood after "oven-drying", thereby resulting in an erroneous moisture content determination. Although this bound water might be extremely difficult to remove by drying, it would be released during the hydrolytic procedure and become a part of the hydrolytic solution. Because of the fundamental pertinence to wood analysis, the persistence of bound water in oven-dried wood samples should be investigated.

It is doubtful that any one of the factors discussed above is responsible for the entire discrepancy from 100% in the mass balances. Rather, it is likely that a combination of a number of these, and/or some unidentified, factors contributed. However, since less than one percent, on average, of the woods remained unaccounted for, the contributions to the mass balance due to these undetermined factors were clearly minimal.

CONCLUSIONS

The goal of this study was a summative analysis method whereby a given wood sample could be analyzed quickly and completely. The Bomb/HPLC summative analysis scheme devised utilizes a bomb vessel for hydrolysis and HPLC for the primary chemical analyses. The use of the bomb vessel allows for the retention of volatiles during the high temperature stage of the hydrolysis while HPLC provides rapid analysis of the hydrolysate solutions.

The absorptivities for the determination of the acid solubilized lignin were obtained by analyzing "reKlasonized" Klason lignin hydrolysates. Although the absorptivities that were calculated using the reKlasonation procedure were approximately fifty percent of those reported in the literature, the experimental method appeared to be sound and the absorptivities substantially correct.

The summative analysis scheme was applied to a series of ten woods; seven were hardwoods and three were softwoods. Using three samples from each wood, the average summative analysis for the group of thirty samples on an unextracted basis was found to be 99.13 ± 0.51%. The range of average summative analyses for the group of ten wood samples was 98.43 to 99.63%. The average summative analysis for the samples on an extractive-free basis was 99.07 ± 0.45%, with a range of 98.31 to 99.60% (average wood values). Several undetermined factors are thought to contribute to the remaining 0.87% (or 0.93%) of the mass balance. These factors include: (1) methanol from cleaved methoxyl groups in the polysaccharides and lignin, (2) dehydration of the lignin during the concentrated acid hydrolysis, (3) trace amounts of polysaccharides moieties, such as rhamnose and fucose, that were present in quantities that were below the detection limit of the analytical method, and (4) experimental error associated with the moisture content determination due to bound water in the comminuted wood that was not removed, and therefore unaccounted. Clearly, the contribution to the mass balance of any one of these factors is small. Furthermore, the complex nature of the interpenetrating system of polymers comprising wood seriously complicates the quantification of these contributions. Thus, the completion of the mass balance to more accurately account for 100% of the starting material becomes increasingly difficult.

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REFERENCES

1. TAPPI: Standards and Suggested Methods, Atlanta, Georgia.

2. W. Moore and D. Johnson: "Procedures for the Chemical Analysis of Wood and Wood Products", U.S. Forest Products Lab., 1967.

3. J. Smelstorius: Holzforschung, 28, 67, (1974).

4. C. Stewart, J. Melvin, S. Tham and E. Zerdoner: Cellulose Chem. Technol., 7, 371, (1973).

5. TAPPI: "New Methods of Measuring Wood and Fiber Properties in Small Samples", TAPPI Press, Atlanta, 1987.

6. W. Kaar: MS thesis, Improved Proximate Analysis of Wood Using HPLC", Univ. Calif., Berkeley. (1987).

7. B. Browning: "The Chemistry of Wood", 65, Interscience Publ., New York, 1963.

8. T. Timell: Wood Science & Tech., 1, 45, (1967).

9. W. Kaar, L. Cool, M. Merriman, and D. Brink: "Complete Analysis of Wood Polysaccharides Using HPLC", submitted for publication to J. Wood Chem. and Tech.

10. W. Kaar and D. Brink: "Simplified Analysis of Acid Soluble Lignin", submitted for publication to J. Wood Chem. and Tech.

11. A. Wacek: Ind. Eng. Chem., 49, 1389, (1957).

12. W. Kaar: Unpublished data.

13. D. Fengel and G. Wegener: "Wood: Chemistry, Ultrastructure, Reactions", De Gruyter, Berlin, 1984.