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Quantitative determination of fatty and resin acids in Kraft black liquors as their trimethylsilyl derivatives by gas chromatography

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Abstract

Tall oil soap is an important byproduct of the Kraft pulping process used at papermaking facilities. Tall oil soap is comprised primarily of the sodium salts of unsaturated fatty acids and a variety of resin acids. These can be recovered from spent black liquor and sold as a feedstock for specialty chemicals manufacture. The ability to monitor the removal of soap from liquor at various stages of the recovery process is of extreme importance to the recovery operation. This paper describes a new procedure which has been developed for the analysis of residual tall oil components in black liquors. In this method, the liquor is extracted with methyl *tert*.-butyl ether (MTBE) under highly alkaline conditions. The extracted components are converted to their trimethylsilyl derivatives, and then analyzed by GC with on-column injection. Quantitation is performed through comparison to an internal standard. This new procedure provides many important advantages over the wet chemical method routinely used for monitoring residual soap levels. These include a more simplified extraction and analysis procedure, an increase in method precision, and detailed quantitative information regarding the type and distribution of components.

Keywords: Resin acids; Kraft black liquors; Tall oil soap; Process monitoring; Fatty acids

1. Introduction

The analysis of wood extractives present in process waters is important for the papermaking industry. The extractives consist of a wide variety of organic compounds which are both monomeric and polymeric in nature. These components are solubilized and transported into waters throughout the papermaking process. Gas chromatography (GC) has been shown to be a useful tool in the qualitative and quantitative evaluation of extractives in certain wood species [1–5] and in a wide variety of paper mill waters [6–14]. Such analyses have proved beneficial in characterizing the dissolved components in mill waters that might eventually lead to pitch deposition and fouling [5–7]. Others have provided information regarding the amounts of toxic components that are present in mill effluents [6–10]. The formation of trimethylsilyl (TMS) derivatives, followed by gas chromatographic analysis with on-column injection, has been shown by Örså and Holmbom [7] to be extremely useful in examining wood extractives in a wide variety of paper mill waters.

Resin and fatty acids are important byproducts of the Kraft process used in the digestion of wood into pulp [11]. The spent cooking solution remaining after the digestion process is known as black liquor. Black liquor is highly alkaline and contains a large

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number of extracted organics as well as the residual inorganic salts required for the digestion, or delignification, of the wood. The resin and fatty acids are present as their sodium salts, and are referred to as tall oil soaps. These acid soaps represent a recoverable raw material in the liquor. The soap can be removed, collected and then sold as a feedstock for specialty chemicals manufacture. The removal of the soap from the spent liquor is accomplished through the phase separation of insoluble soaps, and through evaporative processes, whereby the soap becomes insoluble as the total solids of the liquor increases. The soap floats to the surface in storage and skimming tanks where it is mechanically separated from the bulk liquid. Fig. 1 shows structures (in their acid form) of some of the fatty and resin compounds found in tall oil soap.

The efficiency of the removal of soap from black liquor is extremely important. Any soap that is not removed may eventually deposit as scaling in processing equipment. Also, the solids that remain after the evaporative steps are fed into recovery boilers for heat production. Soap that ends up in the recovery boiler represents a lost economic opportunity for the mill. Because the soap has a lower heat of combustion than the other organic solids in the liquor (lignins, etc.), boiler efficiency can also be compromised.

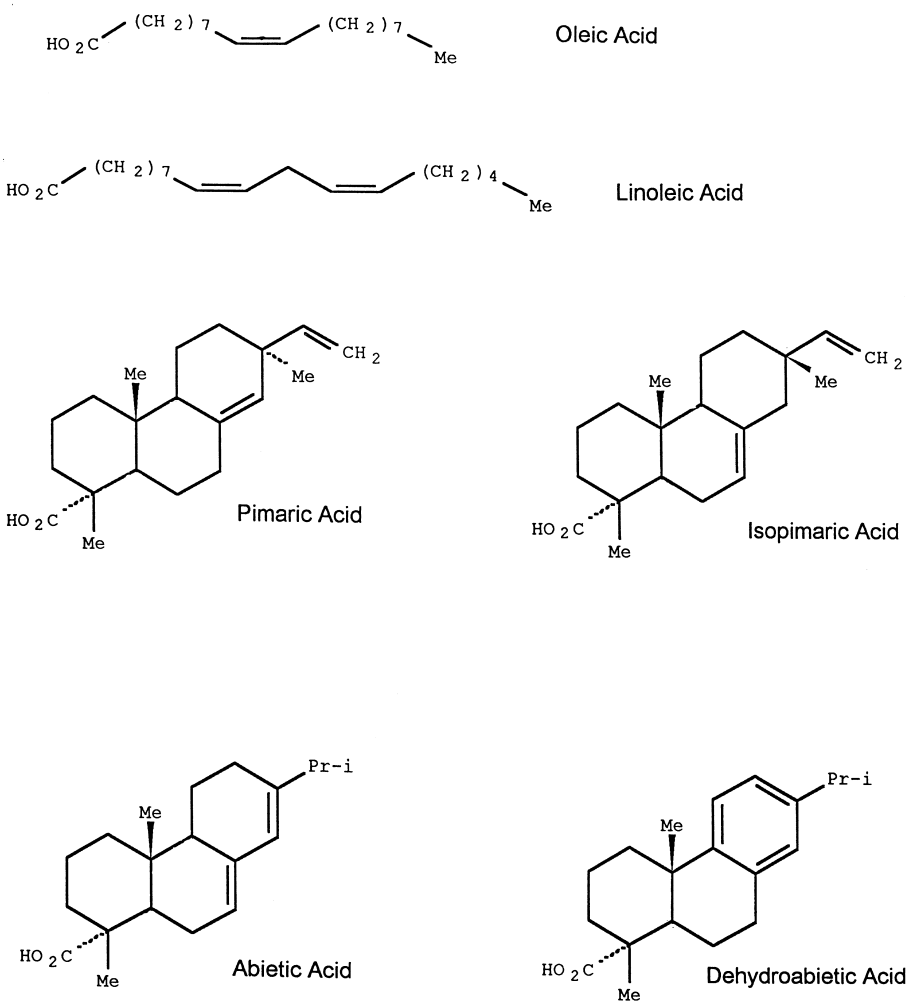

Fig. 1. Structures of fatty and resin acid components typically found in black liquor and crude tall oil.

Monitoring the efficiency of recovery operations can be difficult. Measurement of the residual tall oil components in black liquor after specific processing steps is key in efficiency evaluation. The test procedure commonly used involves acidification and chemical treatment of the liquor, followed by a lengthy, multi-step extraction with different solvent combinations. The extracted tall oil components are isolated via solvent evaporation, and then titrated with standard base. The titration endpoint is determined visually using phenolphthalein as an acid–base indicator. The amount of tall oil components present are expressed as percent tall oil per gram of liquor solids. The method was originally developed by Saltsman and Kuiken as a gravimetric analysis, using the above extraction scheme [12]. The method has since been modified to employ the titration for quantitative purposes, and has been standardized for the pulp chemicals industry [13]. The extraction/titration procedure is commonly referred to in industry as the Buckeye test, in reference to where Saltsman and Kuiken first developed their method (Buckeye Cellulose Corporation).

The Buckeye test is plagued by large sample and solvent requirements, incomplete separation of components and emulsion formation, and lengthy analysis time [14]. The method is prone to errors because of the numerous procedural steps required. In addition, the Buckeye test only provides results that describe the total amount of acids present. No distinction is drawn between the types and distribution of acid species. GC has been used to detect the components present in Kraft black liquors [15–18] and quantitate components in crude tall oil [19,20]. However, to date, a chromatographic method has not been reported for the routine quantitative evaluation of residual tall oil components in spent black liquor.

This paper describes a new method for residual tall oil determination that provides significant improvements over the Buckeye method. The new method employs a simplified extraction procedure requiring a small amount of sample and a single extraction solvent. The extraction is performed under highly alkaline conditions, and serves to isolate the fatty and resin acid components while excluding a significant portion of the other species present. The extracts are converted to their trimethylsilyl derivatives and then analyzed by gas–liquid chromatography with on-column injection. An internal standard is used for quantitative purposes. The extraction and chromatographic separation provides results that give specific information regarding the identity and distribution of components present.

2. Experimental

2.1. Samples and reagents

Samples analyzed in this study were obtained from pulp mills in the southeastern USA and British Columbia, Canada. The liquors were collected from several points within the recovery process. Samples were collected by dispensing black liquor (solids content of approx. 15–50%) directly from the process into water, such that the final liquor solids content was in the vicinity of a few percent [13].

All standards and reagents employed in this study were used ''as is'', without further purification. Extraction solvents [methyl *tert*.-butyl ether (MTBE), methylene chloride, cyclohexane, light petroleum, ethyl acetate] were from EM Science (Gibbstown, NJ, USA), and were of ''Omnisolv'' grade. Spiking solvent (dimethyl sulfoxide, DMSO) was from Burdick and Jackson (Muskegon, MI, USA). The internal standard (heneicosanoic acid, 99+%) was from Aldrich (Milwaukee, WI, USA).

Silylation reagents [bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS)] were from Regis (Morton Grove, IL, USA) and Pierce (Rockford, IL, USA). Fatty acid standards (oleic and linoleic acids, 99+%) were obtained from Aldrich, while resin acid standards were from Helix Biotech (Richmond, Canada). One resin acid standard was a mix of nearly equal amounts of pimaric, sandaracopimaric, isopimaric and dehydroabietic acids. The mixture was prepared by the vendor using compounds that had a reported purity of 99+%, except for the pimaric acid. The pimaric acid had a reported purity of 85–90%, with the remaining 10–15% consisting of sandaracopimaric acid. Single resin acid standards of levopimaric, palustric and neoabietic acids were also used. The reported purity of these were 98, 90–95 and 99+%, respectively.

2.2. Preparation of spiked samples

For extraction efficiency studies, spiked samples were prepared by adding small amounts of concentrated solutions of fatty and resin acid standards in DMSO [8]. The spiked liquor solutions typically contained <1% (w/w) DMSO.

2.3. Sample extraction

A 0.2 g portion of the dilute black liquor was weighed to the nearest 0.1 mg into a 125×15 mm glass culture tube with a threaded top. A 4-ml aliquot of an aqueous phosphate buffer solution (0.05 *M*, pH=11.6) was added to the tube, followed by 4 ml of MTBE. The tube was capped with an aluminum foil lined screw cap and vigorously agitated on a vortex mixer for 30 s. The tube was then centrifuged for a minimum of 5 min at 1500 rpm to break the emulsion between the layers. The top organic layer was transferred via pipette into a 10-ml glass serum vial, which was then placed under a light stream of N_2 gas for drying purposes. The extraction, centrifugation and layer separation steps were repeated twice more using 2 ml of MTBE. The ether portion was added to the serum vial after each extraction. Also added, separate from the extraction process, were 2 ml of a 12.5 μg/ml solution of heneicosanoic acid internal standard in MTBE. The contents of the vial were evaporated to dryness before proceeding to the derivatization step.

2.4. Formation of TMS derivatives

To the serum vial containing the dried extract/internal standard was added 120 μl of BSTFA. The vial was tightly capped with a crimp seal containing a PTFE-lined septum. The vial contents were heated in a block heater at 70°C for 60 min. The 1-h heating time was necessary for complete reaction of the extracts and the internal standard, and this scheme was used for the majority of analyses. It has been found that this time may be decreased by using a mixture of BSTFA and TMCS. A solution of BSTFA–TMCS (2:1) results in complete reaction after a heating time of 20 min at 70°C for MTBE extracts from acidified mill waters [7]. This latter scheme has also been shown to be effective in limited trials in our laboratory on the alkaline extracts. While the use of TMCS as an additional reagent may be useful in decreasing analysis time, the toxicity and potential carcinogenic properties of TMCS may be of concern to some analysts. It is reasonable to assume that commercially available solutions of TMCS (1–10%) in BSTFA might result in complete reaction in less than 60 min. This has not been investigated in our laboratory.

After the heating step, the vial was cooled to room temperature and the contents were transferred to a glass GC autosampler vial containing a glass microvial insert. The autosampler vial was then capped with a septum lined crimp cap.

The internal standard was not present in the solvent during extraction. Initial studies had shown evidence of a variable loss of internal standard when present during the agitation and centrifugation stages. The internal standard was, therefore, added post-extraction and used as a quantitative marker and a check of the operation of the chromatographic system. It was not used in such a way as to mimic extraction behavior of the compounds of interest.

2.5. Chromatographic separation of TMS derivatives

Chromatographic separation was performed using a Hewlett-Packard 5890 Series II Gas Chromatograph, coupled with a Hewlett-Packard 7673 autoinjector, a cool on-column injector inlet, and a flame ionization detection (FID) system. The TMS derivatives in BSTFA were injected neat at a volume of 1 μl.

The column used was open tubular fused-silica, 15 m×0.53 mm I.D., with a dimethylpolysiloxane (DB-1) stationary phase coated at a film thickness of 0.15 μm (J & W Scientific, Folsom, CA, USA). The on-column injector inlet was temperature programmable. It was operated with an initial temperature of 80°C, held for 30 s, and then ramped to 340°C at 100°C/min. The injector was held at the final temperature for 10 min. The column oven was initially 80°C and was held for 1.5 min after injection, followed by temperature ramping at 12°C/min up to 340°C. No hold time was performed at the upper limit. The total run time was approximately 23 min. The flame ionization detector was operated at a

temperature of 340°C. Helium was used as the carrier gas at a flow of 10 ml/min (at 80°C). Detector gases were used at the following flows: H_2 at 40 ml/min, air at 400 ml/min, and He (make-up) at 25 ml/min. Data collection and analysis were performed using PE Nelson Turbochrom data acquisition software.

The parameters described above result in the primary fatty acid (linoleic and oleic) derivatives eluting first as a partially resolved pair, followed by the multiple resin acid derivatives. Peak identities were confirmed using GC–mass spectrometry (MS) of both underivatized and TMS derivatized extracts. A typical chromatogram is presented in Fig. 2. The fatty acids were quantitated by combining the linoleic/oleic areas and comparing versus the internal standard by the usual method. While a small amount of palmitic acid was present in some samples, the area associated with the palmitic acid peak was not included in fatty acid calculations.

All peaks eluting in the time interval between the linoleic/oleic acids and the internal standard were attributed to resin acids. An enlarged portion of the chromatogram in Fig. 2 is presented as Fig. 3, with individual fatty and resin acid components labeled. The GC–MS analyses showed that stearic acid and unsaturated C_{18} fatty acids can, if present, elute immediately following the linoleic and oleic acids and co-elute with the first eluting resin acid. However, the area contributions of these fatty acids did

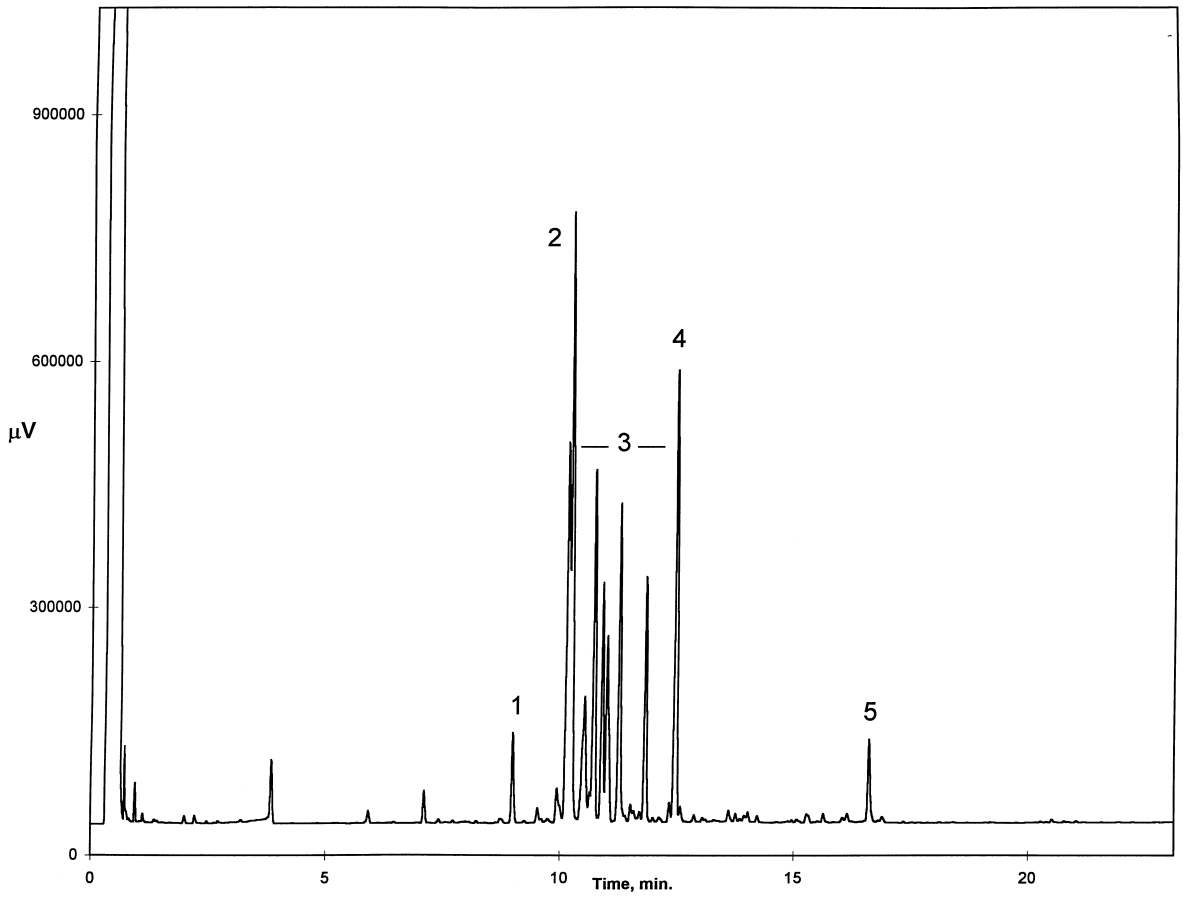

Fig. 2. Chromatogram of the TMS derivatives of components extracted from spent black liquor under alkaline conditions. The liquor was diluted approx. 20:1 with a 0.05 *M* PO_4 buffer, and extracted using methyl *tert.*-butyl ether (4×2×2 ml). Peaks: 1=palmitic acid; 2=linoleic and oleic acids; 3=various resin acids; 4=heneicosanoic acid (internal standard); 5=β-sitosterol.

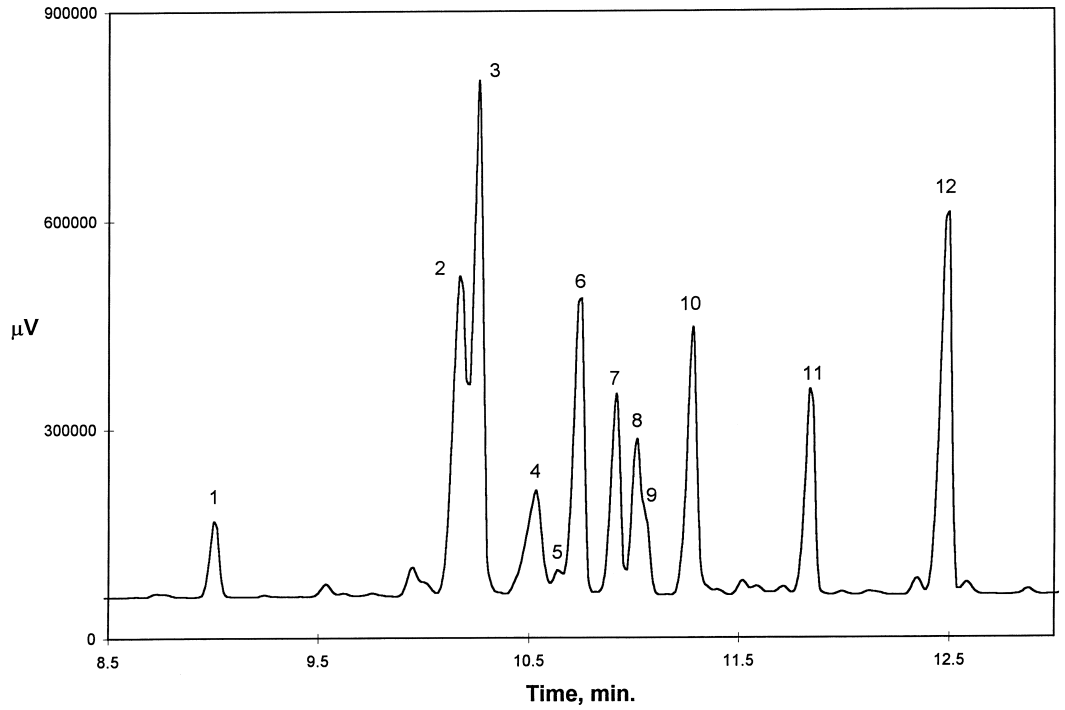

Fig. 3. Expanded view of the fatty/resin acid region of the chromatogram in Fig. 2. Peaks: 1=palmitic acid; 2=linoleic acid; 3=oleic acid; 4=pimaric acid; 5=sandaracopimaric acid; 6=isopimaric acid; 7=palustric acid; 8, 9=co-elution of levopimaric and dehydroabietic acids, respectively; 10=abietic acid; 11=neoabietic acid; 12=heneicosanoic acid (internal standard).

not appear significant in the samples examined. The bulk resin acid peak area was compared to the internal standard also. In this way, quantitative results for fatty and resin acids were generated separately. FID response of the TMS derivatives of the internal standard and the fatty/resin components were measured to be 1.0:1.0. No corrections for detector response differences were necessary. Corrections to the results obtained directly from internal standard comparisons were made based on measured extraction efficiencies.

3. Results and discussion

3.1. Extraction of fatty and resin acids – effect of solution pH

Extraction of lipophilic extractives from process waters is often performed by first acidifying the solution and then extracting the acidic solution with organic solvents. This approach assumes that the optimum extraction will occur when the acids are protonated. However, it has been mentioned in the literature that when fatty and/or resin acids are extracted from certain matrices, higher extraction efficiencies are obtained at slightly alkaline pH [8,9,21]. Initial efforts in the present study centered on examination of the proper pH at which the black liquor matrix should first be adjusted.

When an extract obtained from a diluted liquor initially adjusted to a pH≤2 is analyzed by GC, an extremely large number of components are noted, testifying to the complexity of black liquor composition (Fig. 4). GC–MS analyses have shown that the majority of the compounds eluting in the first few min are small mono- and diacids, along with numerous hydroxy substituted aromatics. Fatty and resin acids are also present. However, the large number of species eluting in the same general time frame

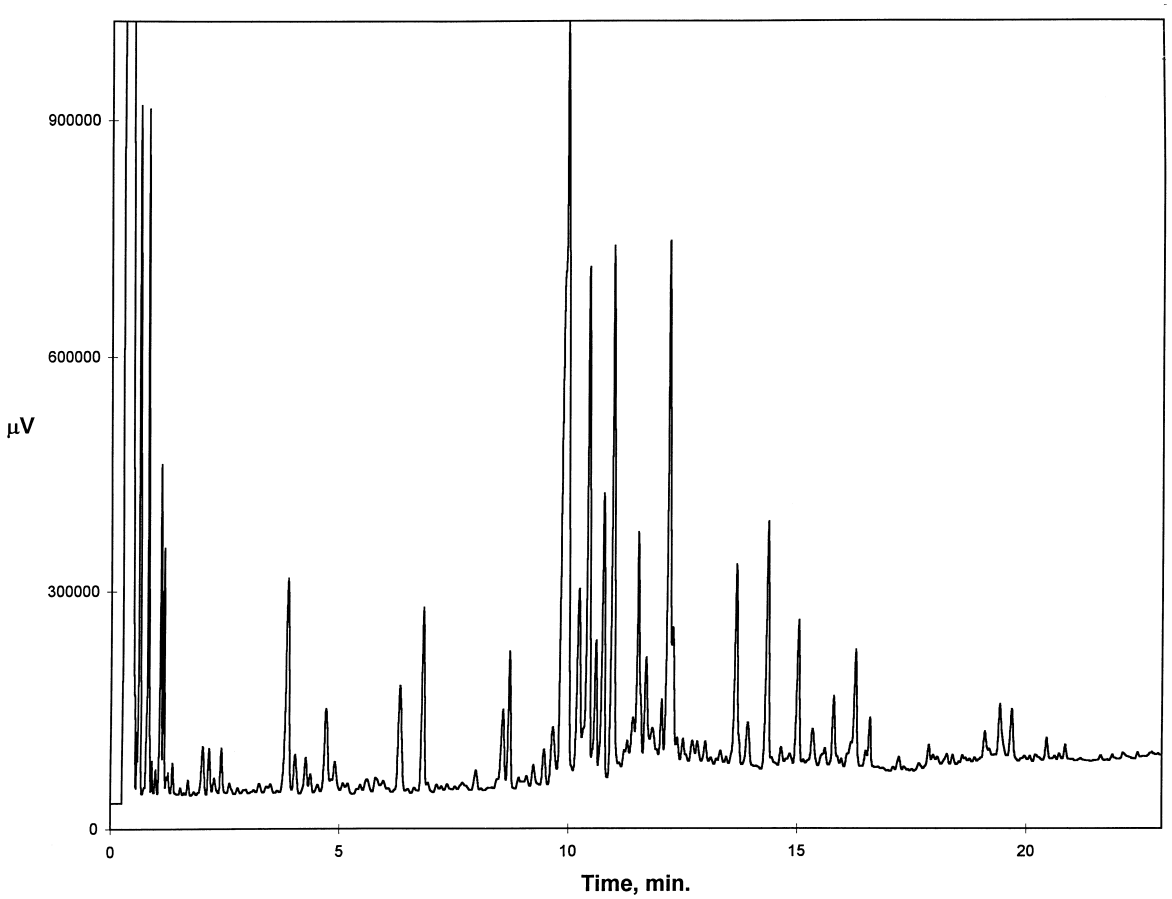

Fig. 4. Chromatogram of the TMS derivatives of components obtained from the acidic extraction of spent black liquor. The liquor (approximately 5% solids) was diluted 20:1 with deionized water and the pH adjusted to 2 prior to extraction with methyl *tert*.-butyl ether.

complicates the integration and quantitation of the residual tall oil components.

The number of components extracted decreased markedly as the pH was increased. GC analysis after neutral pH extraction showed that many of the early eluting peaks were no longer present, and the baseline in the elution region of the tall oil components was better defined. At high pH (>11), the only significantly noted compounds were the major components of tall oil. The dramatic effect of pH on the extraction and chromatographic analysis of the black liquor is seen through comparison of Figs. 2 and 4. The visual appearance of the organic extraction medium during the procedures was very different as well. Under acidic conditions, the ether took on the amber color of the dilute liquor sample. The degree of color in the ether was not as pronounced at intermediate pH. At highly alkaline pH, the ether layer was clear and colorless.

Comparison of peak areas to that of the internal standard showed that the extraction of tall oil components increased with increasing pH. The degree of extraction increased by approximately one-third going from the lowest to highest pH. It was clear that adjustment to highly alkaline pH prior to extraction would be most effective.

Extraction at neutral to slightly alkaline pH posed practical problems as well. At pH~7–9, agitation and centrifugation of the dilute liquor–solvent mixture resulted in a top layer that consisted of a network of

fibrous material, that was not soluble in either the aqueous or organic phases. This web-like structure migrated into the top layer and served to hold the organic solvent stationary, even upon inversion of the tube. The fibrous material could be separated from the solvent through mechanical means, and isolated. Fourier transform (FT) IR analysis of this material revealed structural features consistent with lignin. This suggests that the material might be lignin polymer that precipitates under intermediate pH conditions. Also, when diluted liquor samples were acidified (i.e., pH~2), a brown precipitate formed which either sank to the bottom of the extraction tube or resided at the liquid–liquid interface. It is suspected that the precipitate is highly protonated lignin. The decreased extraction efficiency noted with the acidic liquor solutions may be due, in part, to hydrophobic binding of the fatty and resin acid components to the high-molecular-mass components present. This has been suggested by other researchers [6,8,9,12].

The mechanism of extraction of the unprotonated fatty and resin acids is not completely understood. In the highly alkaline environment of the dilute black liquor, partitioning of the acid salts into an organic phase would not seem likely. One possible explanation is the formation of reverse micellar aggregates. In this scenario, the fatty and resin acids would form assembled structures with the polar head groups aligned at, or penetrating, the surface of an aqueous core. This core contains positive counterions which serve to stabilize the structure. The hydrocarbon portions would reside in the continuous organic medium. Neat black liquor has been described as a normal micellar solution consisting of ionized fatty and resin acids aggregated together with a hydrocarbon core [22]. Outward from this core extend the carboxylate functionalities, which are stabilized by the high ionic strength medium. Perhaps under certain conditions these ionized acids can be partitioned into a bulk organic phase that can accommodate a stabilizing aqueous core. Lignins are expected to be highly ionized in the alkaline aqueous phase, as are many of the small organic components originating from the wood. The ionized fatty and resin acids may resist hydrophobic binding to the lignin due to charge repulsions. The smaller components may still favor residence in the alkaline aqueous medium. Such phenomena may explain why the larger acid salts partition into the ether phase while smaller organics and lignin apparently do not.

3.2. Examination of extraction solvents

MTBE has been shown to be a useful solvent for the extraction of organics from paper mill waters and process streams [7–9,21,23]. It also has an advantage of being less toxic than other commonly used solvents (i.e., methylene chloride). MTBE is safer to use than diethyl ether, as it is less prone to peroxide formation upon storage. MTBE is also easy to work with in that it possesses enough surface tension to allow for convenient transfer with glass pipettes. After the centrifugation step, there is little or no emulsion layer present between the phases. This allows for better quantitative transfer of the organic layer. MTBE is also volatile enough to provide for quick and complete drying under a light stream of air or N_2.

Although MTBE was the first choice for the extraction solvent, other solvents were also examined. Light petroleum, ethyl acetate, methylene chloride, and cyclohexane were investigated as solvents on a specific liquor sample. A comparison of the results for recovered fatty and resin acids versus those obtained using MTBE are given in Table 1.

No solvent studied was as effective as MTBE. Light petroleum and cyclohexane were the poorest performers. The light petroleum results were particularly interesting, as that solvent is the primary organic solvent used in the acidic Buckeye extraction. Methylene chloride was somewhat effective. However, under the experimental conditions its use was impractical due to the solvent density. The $MeCl_2$ layer was at the bottom of the extraction tube and transfer to another vessel was difficult. In

Table 1
Comparison of extraction solvents

Solvent	Extraction efficiency relative to MTBE	
	Fatty acids	Resin acids
Methylene chloride	0.87	0.57
Cyclohexane	0.24	0.20
Light petroleum	0.17	0.12

Results are presented as recovery relative to MTBE.

addition, emulsion formation and stability was noted more with $MeCl_2$ than for MTBE or other solvents.

Results were not obtained for ethyl acetate. After agitation and centrifugation, the same type of suspected lignin material migrated into the ethyl acetate layer as was observed with MTBE at intermediate pH. Although ethyl acetate has been described as an effective extraction solvent for fatty and resin acids [9,23], it is not a practical choice for this analysis.

It is interesting to note that the extracting abilities of the solvents follows the same trend as their abilities to solubilize water. This factor supports the idea that water stabilized aggregates may play a role in the extraction of the acid salts into the ether phase.

3.3. Extraction efficiency of MTBE

In order to facilitate meaningful quantitative results, the extraction efficiency of MTBE under the experimental conditions needed to be established. To accomplish this, a large number of black liquor samples were first spiked with small aliquots of concentrated solutions of known fatty and resin acid standards. The fatty acid spiking solution contained high purity oleic and linoleic acids, in relatively equal amounts. The resin acid spiking solution contained a mixture of four separate compounds. These were pimaric, isopimaric, sandaracopimaric and dehydroabietic acids. The spiked liquors were then analyzed alongside their unspiked parent liquor. The amount of fatty/resin acid recovered was calculated as the difference between the results for the spiked and unspiked samples. The percent recovery was calculated by taking the ratio of the amount recovered to the amount spiked and multiplying by 100. A number of liquor samples were also spiked with pure DMSO and analyzed in an identical fashion. The presence of the small amount of DMSO was found to have no significant impact on the extractions.

The liquors examined in the extraction efficiency study came from a number of pulp mills in the southeastern USA and British Columbia, Canada. In this way, the extraction was examined on liquors originating from the pulping of different wood furnish blends. In addition, the liquors were sampled from various parts of recovery processes. This resulted in liquors with highly variable amounts of residual tall oil present. The liquors also contained variable amounts of dissolved total solids.

Table 2 shows the data and recoveries, along with a statistical summary of the results. For each of the trials, the mass of liquor used was corrected for the amount of DMSO present, so that the amounts of spike added and recovered were based only on the amounts of acid standard and liquor used in the sample preparations. The average fatty acid extraction efficiency is 96.2%. The average resin acid extraction efficiency is somewhat less, at 79.2%. A difference in fatty and resin acid extraction with MTBE has been noted elsewhere in the literature for mill water effluents at slightly alkaline pH [8]. No significant difference was observed for the extractions with respect to total solids, original wood furnish, total acid content, or process point sampled.

Using a slightly smaller data set (14 pairs of spiked and unspiked liquors), the effect of using larger volumes of MTBE was examined. Using 4-ml aliquots of solvent for each of the three extractions resulted in similar fatty acid recovery (97.8%) and slightly higher resin acid recovery (87.6%) when compared to the original procedure. The use of larger volumes slightly increases sample preparation time (increased drying time), but either extraction scheme can be used as long as the proper extraction efficiencies are taken into consideration.

To further investigate the extraction process, a solution of fatty and resin acid standards was prepared in the pH 11.6 buffer with a small amount of residual alkalinity added to enhance solubility. The concentration of the solution was ~200 ppm each in oleic and linoleic acids, and ~250 ppm in total resin acids. A 0.2-g aliquot of this solution was diluted, extracted (4×2×2 ml MTBE) and analyzed. The fatty and resin acids were found to extract at 100 and 85%, respectively. This shows that the combination of pH and solvent composition is key in the extraction process. This also lends further credence toward the theory that some type of aggregation behavior independent of the sample matrix might play a role in the partitioning of the components into the organic phase.

3.4. Precision

The method precision was evaluated by one

Table 2
Spike recovery data for liquor samples extracted using MTBE under alkaline conditions

Sample No.	Sampling point	Percent solids	ppm Fatty acid spiked	ppm Fatty acid recovered	% Fatty acid extraction	ppm Resin acid spiked	ppm Resin acid recovered	% Resin acid extraction
1	FW	1.8	112	102	91.1	103	71.0	68.9
2	FW	1.8	234	216	92.3	214	161	75.2
3	TSS	6.6	10.2	10.0	98.0	56.6	50.2	88.7
4	TSS	6.6	66.3	62.7	94.6	159	132	83.0
5	TSS	6.0	267	265	99.3	450	342	76.0
6	TSS	6.0	479	483	100.8	912	735	80.6
7	50%	5.3	267	268	100.4	277	240	86.6
8	50%	5.3	538	514	95.5	470	379	80.6
9	TSS	7.0	278	266	95.7	295	228	77.3
10	TSS	7.0	459	453	98.7	550	442	80.4
11	FW	3.5	90.6	91.0	100.4	460	359	78.0
12	FW	3.5	286	278	97.2	295	228	77.3
13	FW	3.2	190	194	102.1	306	241	78.8
14	FW	3.2	370	373	100.8	521	417	80.0
15	TSS	4.3	43.2	41.0	94.9	39.6	31.7	80.1
16	TSS	4.3	89.1	85.2	95.6	81.5	64.7	79.4
17	FSS	5.8	104	94.4	90.8	108	94.0	87.0
18	FSS	5.8	184	169	91.8	191	166	86.9
19	FW	6.1	128	109	85.2	117	75.4	64.4
20	FW	6.1	222	211	95.0	203	153	75.4
21	FW	6.1	119	118	99.2	109	86.2	79.1
22	FSS	5.9	115	108	93.9	105	78.7	75.0
23	FSS	5.9	220	216	98.2	202	166	82.2
				Average	96.2		Average	79.2
				S.D.	4.1		S.D.	5.6

Abbreviations for process sampling points are as follows: FW=outlet from pulp washer; TE=inlet to evaporator; TSS=inlet to soap skimmer; FSS=outlet from soap skimmer; 50%= outlet from 50% solids tank.

operator analyzing three different liquor samples nine times each. Each analysis was the result of a separate sample preparation. The total acid content varied significantly between the three liquors. The results and statistical evaluation for each set are given in Tables 3–5. The fatty and resin acid concentrations were calculated using corrections based on the average extraction efficiencies from Table 2.

With the exception of the resin acid values for the lowest concentration sample, all of the relative standard deviations (R.S.D.s, equal to the standard deviation·100/average value) are ≤2.0%. The larger variation seen for the resin acids in the low concentration sample may be due to variable extraction at such a low level. The resin acid precision is considerably better for more concentrated samples. The precision of results for total tall oil content is dependent upon the individual precision for each group. While the total acid precision appears poorer for the lowest concentration sample, it should be noted that the sample resin-to-fatty acid ratio is ~5:1. In this case, the variation in total acid content is heavily weighted by the resin acid variability. For a sample where the total acid content is very low, an improvement in precision would be expected when there is less disparity between resin and fatty acid content.

When the efficiency of soap removal is being evaluated in industrial settings, test results are described in terms of the percentage of tall oil components present per gram of liquor solids. Tables 3–5 also display the precision data expressed in these units.

3.5. Comparison with other methods

Fig. 5 shows chromatograms of a liquor residue

Table 3
Precision data obtained on a liquor sample containing approximately 140 ppm total fatty and resin acids (low concentration sample)

	Average (ppm)			Tall oil per g of liquor solids (%)
	Fatty acids	Resin acids	Total acids	
	23.6	120	144	0.217
	22.9	117	140	0.213
	23.0	119	142	0.215
	23.1	123	146	0.221
	22.8	114	137	0.207
	23.1	116	139	0.211
	22.9	111	134	0.203
	22.8	113	136	0.205
	23.1	113	136	0.206
Average	23.0	116	139	0.211
S.D.	0.241	3.86	4.00	0.00606
R.S.D. (%)	1.05	3.32	2.87	2.87

The results in the last column have been calculated based on 6.6% (w/w) solids.

that was from alkaline extraction with MTBE, and a residue obtained from the same liquor using the acidic Buckeye extraction. The profiles are very similar, although there appear to be some differences in the resin acid region. Resin acids have been reported to experience isomerization upon heating or exposure to mineral acids [24]. As the two extraction procedures are carried out at vastly different pH values, the resin acid species in existence after the extraction may differ. Also, it may be possible for these isomerization reactions to take place in the chromatographic system at the temperatures employed. For several black liquor samples, the residues obtained from the Buckeye extraction procedure were profiled. In each case, the fatty acid/resin acid peak ratios were identical to those obtained using the alkaline MTBE extraction technique.

There are few quantitative methods reported for the determination of tall oil in black liquor. While the Buckeye procedure is useful in monitoring the soap removal in recovery processes, it is hampered by the problems previously discussed. The precision of the

Table 4
Precision data obtained on a liquor sample containing approximately 1200 ppm total fatty and resin acids (intermediate concentration sample)

	Average (ppm)			Tall oil per g of liquor solids (%)
	Fatty acids	Resin acids	Total acids	
	330	857	1187	3.39
	331	855	1186	3.39
	335	868	1203	3.44
	334	874	1208	3.45
	336	878	1214	3.47
	332	869	1201	3.43
	336	878	1214	3.47
	336	888	1224	3.50
	335	909	1244	3.55
Average	334	875	1209	3.45
S.D.	2.20	16.4	17.9	0.0512
R.S.D. (%)	0.66	1.87	1.48	1.48

The results in the last column have been calculated based on 3.5% (w/w) solids.

Table 5
Precision data obtained on a liquor sample containing approximately 2900 ppm total fatty and resin acids (high concentration sample)

	Average (ppm)			Tall oil per g of liquor solids (%)
	Fatty acids	Resin acids	Total acids	
	993	1882	2874	4.79
	988	1870	2858	4.76
	999	1903	2902	4.84
	1035	1959	2994	4.99
	1019	1940	2959	4.93
	1022	1953	2975	4.96
	999	1902	2901	4.84
	1018	1928	2945	4.91
	1036	1989	3025	5.04
Average	1012	1925	2937	4.90
S.D.	17.9	39.1	56.7	0.094
R.S.D. (%)	1.77	2.03	1.93	1.93

The results in the last column have been calculated based on 6.0% (w/w) solids.

Buckeye method, when performed by well trained and highly experienced operators, has been estimated to have a R.S.D. of ~1.5% [25]. Comparison of this uncertainty with the precision estimates noted in Tables 3–5 shows that the method of this study and the Buckeye can be performed with similar precision. However, the multiple sample preparation, extraction and analysis steps performed in the Buckeye method lend themselves to multiple sources of errors, and the propagation thereof. With such a highly technique-dependent method, these problems will be more noticeable with less experienced operators. The Buckeye method employs a colorimetric titration endpoint that is difficult to distinguish, and systematic errors can result as well. This will be discussed later in this section.

A distinct advantage of the GC method is its ability to provide information regarding the amounts and distribution of individual fatty and resin acid components. As the Buckeye method determines total acid, it is not capable of component differentiation. The ability to separately characterize fatty from resin acids may be useful in better understanding recovery operations and treatment programs, and in assessing the composition and quality of recovered tall oil.

Direct comparisons of the results from the GC method and those from the Buckeye method are given in Fig. 6 and Table 6. The data represent the analysis of 14 different black liquor samples as analyzed in our laboratory using the GC method, and at four separate outside laboratories using the Buckeye method. The GC results are consistently lower than those obtained using the Buckeye procedure. Differences between GC and Buckeye results are most significant for samples where the residual tall oil content is low. It is suspected that this bias may be due to a systematic difference in the way that the endpoint of the colorimetric titration is determined. The endpoint in the Buckeye method is the color transition of phenolphthalein from colorless to a pink, persistent for 30 s. The perception of this color change can be perturbed by the color of the analysis solution. This can lead to an excess of titrant required to achieve the perceived color change, and falsely high results. Differences due to endpoint errors will not be as noticeable when high levels of tall oil components are present. However, as the tall oil levels decrease, the corresponding titrant volumes required to reach the endpoint decrease. At very low levels, a variation or bias in endpoint determination will be a significant source of error. At these low concentrations the variation or bias in titration volume is large compared to the overall titrant volume consumed. For example, if a sample contains 0.35% tall oil per gram of liquor solids, and the total solids content is 5% (w/w), the theoretical titrant volume is only 1 ml. Just a small number of drops in excess of the true endpoint will result in a large positive error.

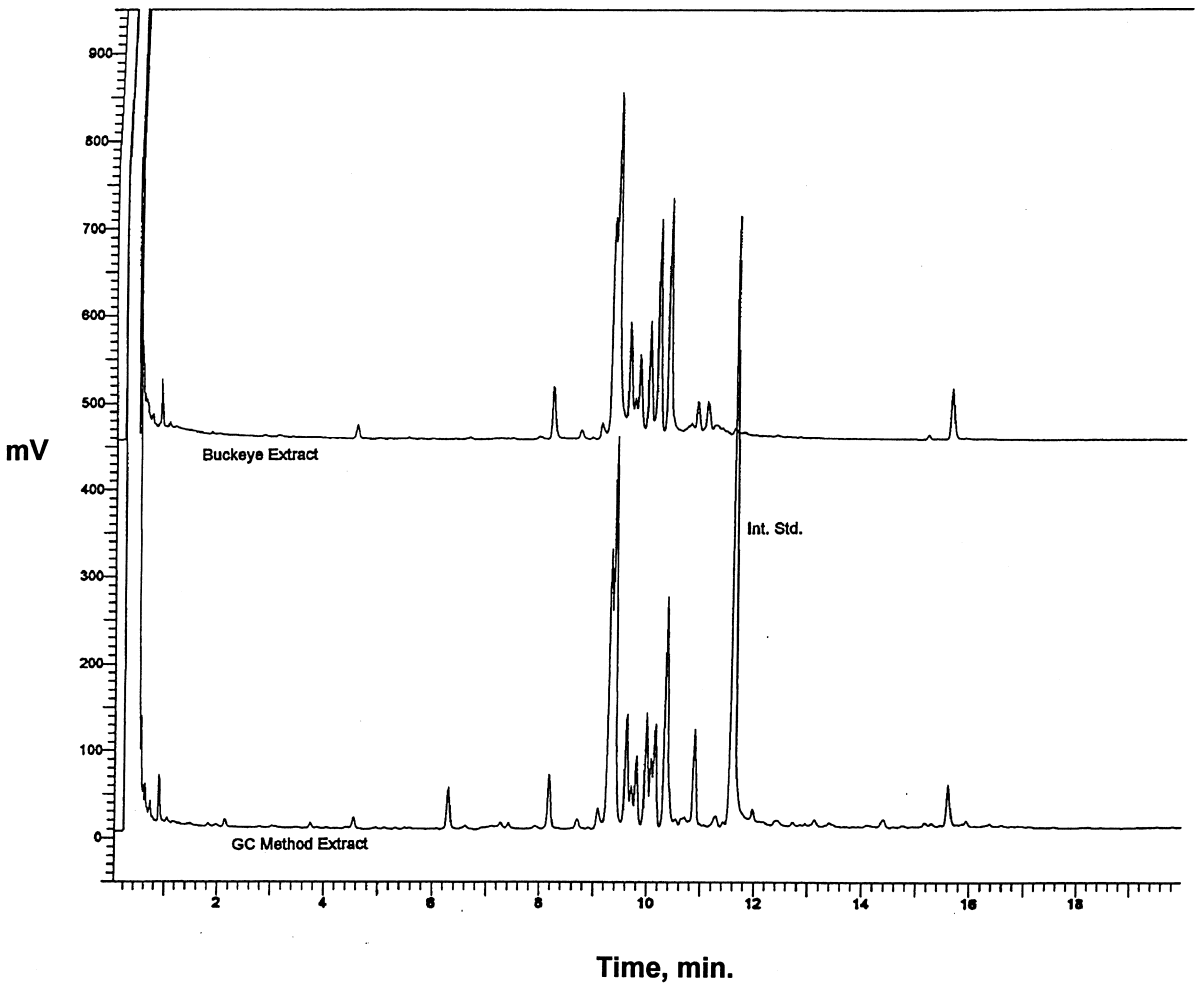

Fig. 5. Comparison of chromatographic profiles of two separate extracts from the same black liquor sample. The top chromatogram is of the TMS derivatives of components obtained using the extraction procedure of the Buckeye method (Ref. [13]). The bottom chromatogram was obtained using the alkaline MTBE extraction procedure of this study.

Another source of error in the Buckeye method is centered around an assumption regarding tall oil composition. The mass of acid species present is determined by comparing the volume of titrant consumed with the acid number of the crude tall oil soap that has been separated and removed from the liquor. The acid number used can be either an assumed value (160 mg KOH equivalents per g in Ref. [13], but often assumed to be 172 in practice at industrial facilities) or one determined by titrating the recovered material. The basis of using the acid value in the calculations is to account for the fatty to resin acid ratio and the amount of non-saponifiable material present in the soap. However, using a value directly related to the recovered tall oil components assumes that the fatty to resin ratio, and percentage of non-saponifiables, in the residual tall oil are the same as those in the recovered material. Analyses in our laboratory of black liquors reveal that the fatty to resin acid ratio of the residuals can be different at various points in the recovery process. Fatty acid has been measured in our laboratory to make up 30–40% of the total acid components in liquor samples prior to significant soap removal. However, when liquors are sampled after soap skimming tanks, they are found to contain as little as 10–15% fatty acid. The

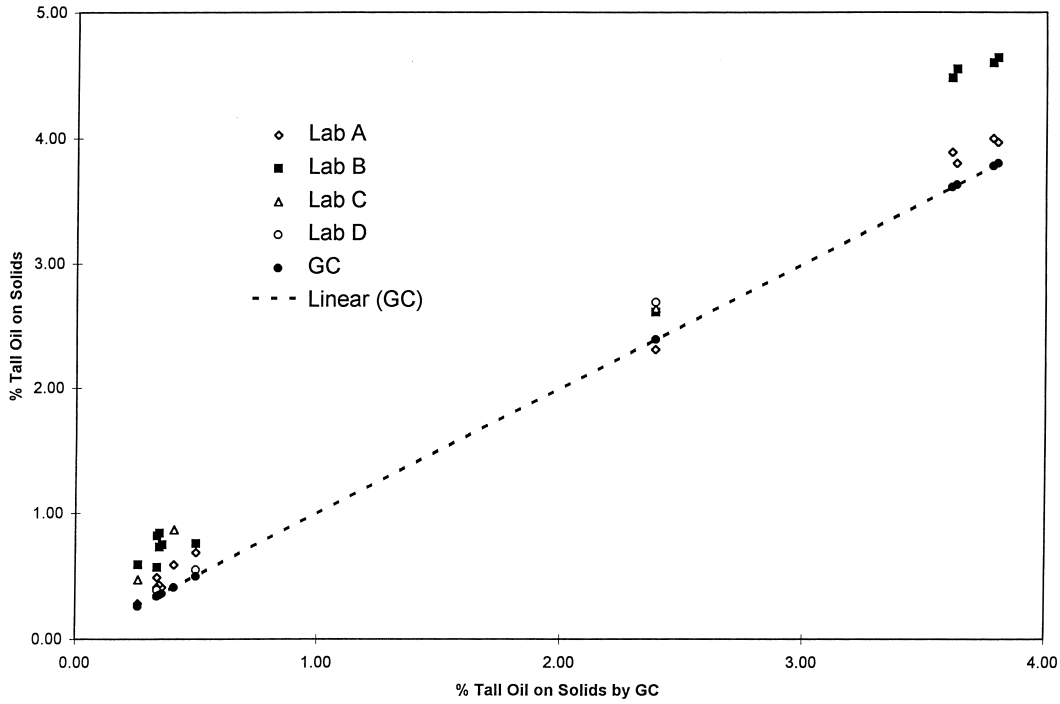

Fig. 6. Plot of the results of this study (GC) vs. those obtained on the same samples at outside laboratories (Buckeye). All Buckeye results were calculated using an acid number of 172 mg KOH per g of tall oil.

discrepancies and variations of acid species in residual liquors make the use of a calculated or assumed acid number less reliable. The use of the GC method eliminates these problems because the amounts and distribution of fatty and resin acid species are determined directly.

Table 6
Comparison of results obtained by outside laboratories using the Buckeye procedure and results obtained using the method of this study

Sample No.	Tall oil on liquor solids (%)				
	GC	Laboratory A	Laboratory B	Laboratory C	Laboratory D
1	2.39	2.31	2.61	2.64	2.69
2	0.26	0.28	0.59	0.47	0.26
3	3.78	4.00	4.60		
4	3.80	3.97	4.64		
5	3.61	3.89	4.48		
6	3.63	3.80	4.55		
7	0.35	0.38	0.73		
8	0.36	0.41	0.75		
9	0.35	0.43	0.84		
10	0.34	0.41	0.82		
11	0.41	0.59		0.87	
12	0.50	0.69	0.76		0.55
13	0.34	0.49	0.57		0.39
14	9.36	10.24		8.87	

All Buckeye results were determined assuming the tall oil in the liquor to have an acid number of 172 mg KOH/g.

4. Conclusions

A simple extraction procedure has been developed to isolate tall oil components from spent Kraft black liquor. The extract is derivatized and analyzed using GC with on-column injection and FID. This method provides information regarding the composition and concentration of fatty and resin acids that is more detailed than that obtained using the industry standard test. This new procedure should prove useful in the analysis and characterization of liquor at various stages of tall oil soap recovery processes. The procedure also shows promise in aiding the evaluation of treatment programs intended to enhance the separation and recovery of tall oil soaps from spent black liquors. In addition, the procedure can be adapted for use in the characterization of crude tall oil obtained from further processing the soap. This may prove beneficial in the quality control of tall oil and associated products.

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