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effluents and foams

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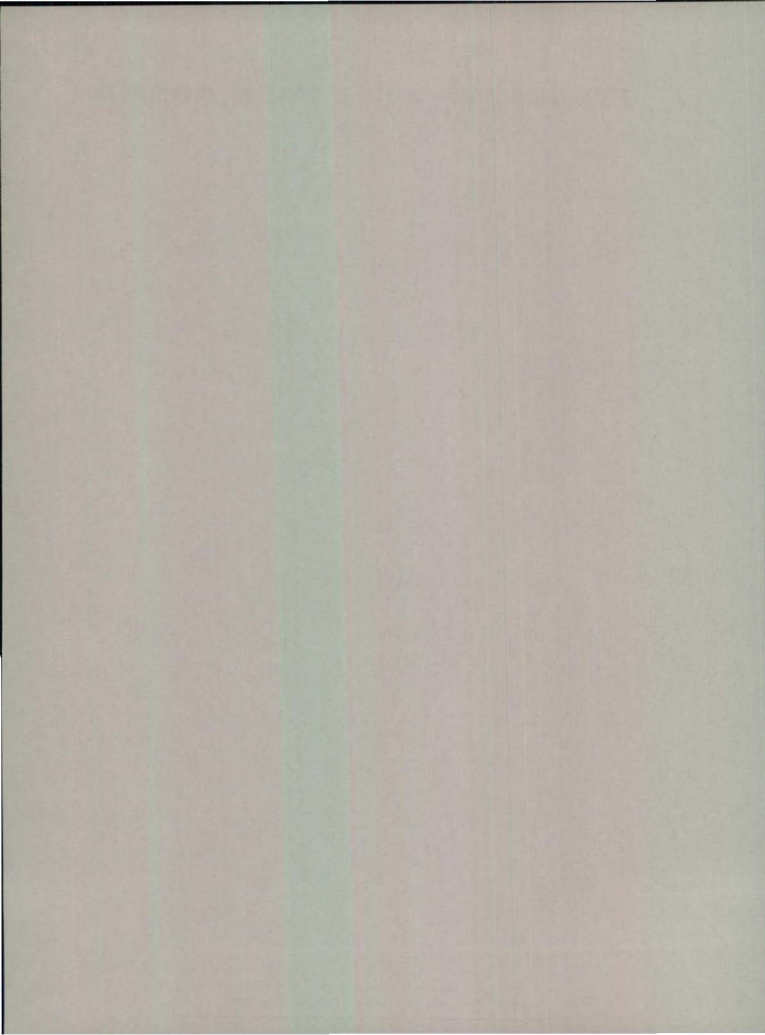
Establishment

Biological Station
St. Andrews, N. B.

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ABSTRACT - The concentration of resin acids, determined by the reaction with acetic anhydride in sulfuric acid, is 21-23 mg/l in sulfate and 34 mg/l in groundwood mill effluent. The main source of resin acids in the former is the debarker effluent, which contains 62-180 mg/l of resin acids. The concentration of resin acids in foams from the sulfate mill is 28-127 mg/l. Additional organic compounds were isolated from the effluents in the form of petroleum ether, ether, carbon-chloroform (CCE) and carbon-ethanol (CEE) extracts. The concentrations of these fractions in the effluents follow generally the patterns of resin acids. The groundwood mill effluent contains an acidic polysaccharide, 230 mg/l. Concentration of fiber in this effluent is 10 g/l. The fiber contains approximately 1 g/l of extractives, including 182 mg/l of resin acids. The fractions isolated from the effluents were characterized by UV, IR, and fluorescence spectra. Preliminary data on the toxicity of the fractions to Atlantic salmon parr indicate a decrease of toxicity with increasing polarity of the fractions.

Introduction

This report deals with sulfate and groundwood mill effluents. The sulfate pulping process is based on the digestion of wood with a mixture of sodium sulfide and sodium hydroxide to dissolve lignin and other non-cellulosic materials. As the name indicates, the groundwood process is based on the mechanical disintegration of wood and no chemicals are used in the disintegration process. The total effluent from both pulping operations consists of several streams with quite different composition. Wet debarking, used in both processes yields an effluent containing bark extractives, mainly resin and fatty acids. From 96 to 98% of the spent sulfate cooking liquor (black liquor) is removed from the pulp and regenerated so that only 2 to 4% of the spent liquor reaches the sewer. Major part of water pollution generated by the sulfate pulping process originates in the digester condensates, containing volatile and steam-distillable compounds. Bleaching of the pulp is another source of effluent. Sulfate pulp is bleached by a multi-stage process including chlorination, sodium hydroxide washing, and chlorine dioxide treatment. The purpose of this treatment is to remove coloring materials from the pulp. The aim of groundwood pulp bleaching is to decolorize the pulp without actually removing the colored materials from the pulp. Peroxides and/or zinc hydrosulfite are used in this process. Of the bleaching chemicals, chlorine dioxide is prepared on the premises from sodium chlorate. The acidic effluent from this process is usually combined with the black liquor. Larger sulfate mills may also have their own chlorine-caustic soda plants. Both sulfate and groundwood mills use slimicides to preserve the pulp and to prevent the growth of slime-producing bacteria in the plant equipment. For a more detailed description of the pulping technology see (1-4). A review of slimicides used by pulp and paper industry is presented in (5).

Resin acids

Coniferous trees contain a resinous material which during sulfate pulping can be recovered in the form of tall oil. Tall oil contains approximately 45% of resin acids, 45% of fatty acids, and 10% of neutral material (phytosterols, higher alcohols, and hydrocarbons). The recovery of tall oil is economical only from trees rich in resin such as Southern Pines. Tall oil production in the U.S.A. is in the order of about one billion lb/year. Tall oil resin acids are used for sizing paper and in surfactant manufacture, tall oil fatty acids serve as ingredients of protective coatings, soaps, surfactants, flotation agents, and are also used as chemical intermediates. Tall oil is usually not recovered in northern U.S.A. and in Canada and the components of tall oil appear in

the effluent. For a review of the commercial uses of tall oil see (6,7). Tall oil fatty acid fraction contains 72-94% of unsaturated fatty acids, mainly oleic and linoleic acid. Saturated fatty acids present are mainly palmitic, stearic, and arachidic acid (7,8). Resin acids are diterpene acids with structural formulae given in Figure 1.

Chemical properties of resin acids are reviewed in (9,10). Levopimaric, abietic, and neoabietic acid have two conjugated double bonds and both levopimaric and neoabietic acid can be isomerized in acid medium to give abietic acid. Dehydroabietic acid contains benzene ring in the molecule and has therefore the reactivity of an aromatic compound. Abietic-type acids are oxidized easily to give peroxides as intermediates, and di- and tetrahydroxy acids as final products. IR spectra of resin acids are described in the literature (11,12).

Abietic acid gives a color reaction with acetic anhydride in sulfuric acid and this reaction was used to determine resin acids in pulp and paper mill effluents (13). A sulfonation reaction is used for the determination of dehydroabietic acid (14). A color reaction of abietic acid with 1-amino-2-naphthol-4 sulfuric acid was recently described (15).

Thin-layer chromatography of resin acid methyl esters on silica gel, using 95:5 v/v mixture of white spirits and ether was described (16). Gas chromatography on 20% DEGS or 5% Versamid 900 on Chromosorb W gives a good separation of resin acid methyl esters (17,18), and the method was used to determine resin acids in sulfite and sulfate mills effluents (19). Abietic and dehydroabietic acid were found to be the main resin acids in the sulfate mill effluent and were present in a concentration of 2.3-2.5 mg/l. The gas chromatographic method gave higher results than the acetic anhydride-sulfuric acid method.

Little is known about the biodegradation of resin acids. A ketone was isolated from the products of microbial degradation of dehydroabietic acid (20). Resin acids are toxic to fish at concentrations of about 1 mg/l (13).

Phenolic substances

Most of the phenolic compounds in pulp mill effluents are derived from lignins and tannins. Compounds such as vanillin, acetovanillone, vanillic acid, ferulic acid, hydroferulic acid, p-hydroxybenzoic acid, and p-hydroxycinnamic acid are slightly toxic to fish (21,22). Phenolic compounds may, however, be chlorinated during the bleaching to yield much more toxic products. This has been confirmed by the isolation of tetrachloro-o-benzoquinone from the bleached sulfate chlorination effluent. This compound causes 100% mortality of

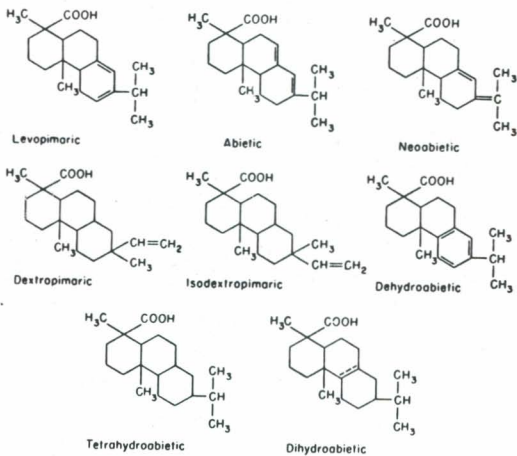


Fig. 1. Structural formulae of most common resin acids.

young salmon in 10 h at a concentration of 3 mg/l (23). UV spectra and ionization-difference spectra of fractions of bleach effluents have been described (24). No individual compounds were isolated in this study.

An alcohol, 4-(p-tolyl)-1-pentanol (I), was isolated from the low-vacuum stage condensate of the weak black liquor evaporator, and indications were obtained that other toxic compounds are present. I is quite toxic to fish and it is interesting to note that its cytochrome-oxidase inhibitory activity rivals that of the cyanide ion (25).

Lignin

Lignin could be classified as a phenolic compound since its molecule is based on propyl guaiacol units, but differs in many respects from the simple phenolic compounds, described in the previous chapter. Lignin is a macromolecular substance with molecular weight of the order of several thousand, which in wood acts as an adhesive, binding the fibers of cellulose. Lignin liberated from groundwood corresponds essentially to the native wood lignin, but has somewhat lower molecular weight. In sulfate cooking of wood, lignin is degraded by the action of sulfide to yield products of low molecular weight and sulfate lignin, containing about 2% of sulfur (26,27). Only a small amount of these products reaches the sewer and the major part is burned in the recovery furnace. In contrast to the groundwood operation, where virtually all liberated lignin compounds are discharged in the effluent, in the sulfate pulping the principal source of lignin material is the bleach effluents. Some attempts to chemically characterize lignin compounds in bleach effluents have been made with little success (24,28) and it was suggested that the color of the sulfate chlorination effluents is due mainly to carbohydrate degradation products. A comprehensive review of the reactions of lignin during pulping has been recently published (29).

UV spectrophotometry is useful for the characterization of lignin material in groundwood effluents. Differential UV spectra of phenols in acid and alkali have been described (30) and the spectrum of lignin was interpreted in these terms (31,32). Spectra of lignin preparations containing sulfur are practically identical with those of natural lignins (33).

IR spectra can be used to distinguish between hardwood and softwood lignins. Hardwood lignin has an absorption band at 835-842 cm^{-1} , while a similar band occurs at 822-825 cm^{-1} in softwood lignin (34).

UV and IR spectra were used to study the degradation of lignin by UV light (35). The data indicate that lignin is degraded by a free-radical mechanism.

A study of chlorination of pine sulfate lignin (36) revealed a total yield of aromatic chlorine substitution in the order of 3-4% of applied chlorine. Most of the substitution occurred in the 5- or 6-positions of the aromatic rings. Disubstitution took place only to a minor extent. Lignin was extensively oxidized by aqueous chlorine. IR absorption bands at 1620 and 1720 cm^{-1} (o-quinone and C=C), an increase in acidic group content, and apparent absence of aromatic character were found in a chlorolignin preparation containing about 10% Cl (37).

UV data indicate that the residual lignin in pulp is different from that in liquor (38,39).

Sulfur compounds in sulfate mill effluents

Volatile sulfur compounds such as methyl sulfide, dimethyl sulfide, and dimethyl disulfide reach the effluent of sulfate mills mainly from the condensates and their amount varies from 1 to 14 kg/ton of pulp (40,41). The effects of cooking variables on the formation of organic sulfur compounds during pulping of pine has been studied (42). A method for the determination of methyl sulfide, dimethyl sulfide and dimethyl disulfide by gas chromatography, after stripping with nitrogen from aqueous solution, has been described (43). Symptoms of poisoning of fish by these compounds have been observed (40). The toxicity of volatile sulfur compounds is quickly neutralized by dilution, and from the pollution standpoint they are probably less important than wood, bark, fiber, and suspended carbohydrate compounds of the effluent which accelerate bacterial sulfate reduction and the production of much more toxic hydrogen sulfide (44,45).

Foaming of pulp mill effluents

The volume and stability of foam, produced by different sulfate pulp and newsprint effluents, have been studied (46). In a bleached sulfate operation, the main cause of foam is the caustic extraction washer effluent, particularly when mixed with chlorination and calcium hypochlorite washers. Black liquor also foams extensively in mixtures with these effluents and with sea water. On the other hand, zinc hydrosulfite effluent reduces the stability of foams and a similar effect is observed with the green lignin dregs. The appearance of dark resinous material on the surface of foams suggests the possibility of the extraction of some organic material by the foam from the solution.

Toxicity of pulp mill effluents to aquatic animals

Numerous papers on the toxicity of sulfate mill effluents to fish have been published. The effluents are complex mixtures of organic and inorganic compounds, variable in composition from mill to mill and within the same mill. It is generally accepted that the effluents cause a deterioration of the receiving waters, such as increase in dissolved and suspended solids and oxygen depletion.

Resin acids (19), tetrachloro-o-benzoquinone (23), and sulfide (47) are very toxic to fish. No relation was found between the toxicity of an effluent and its content of sulfides and mercaptans and a slight relation (48), and no relation (49) was found between the toxicity and BOD.

Sublethal effects of the effluents and avoidance reactions of aquatic animals are very likely ecologically more important than lethal effects of the effluents. Chinook salmon is reported to avoid 5 and 10% and to prefer 1.25% concentration of the effluent, whereas 2.5% was attractive in December and repellent in August and September (50). Atlantic salmon parr avoided moderately the effluent in the whole range of concentrations studied (10 ppm - 10% (51)). Survival of lobster larvae was not affected at concentrations below 10% (52), and concentrations up to 20%, introduced 50 cm upstream from resting lobsters, did not elicit behavioural responses (53).

Exposure of Sparus macrocephallus to sublethal concentrations of sulfate effluent caused a decrease of glycogen in hepatic cells, a decrease of RNA in the pancreas, and necrosis of intestine epithelium (54). Respiratory abnormalities of fish, with a minimum concentration response of 1% in pulping effluent and 4% in bleaching effluent, were reported (55).

Effects of groundwood pulp fibers on fish and fish eggs were reported. Impaired oxygen uptake and swimming ability, and a decrease in active metabolism were reported at fiber concentrations of 50-150 mg/l (56).

This report describes the determination of resin acids in sulfate and groundwood mill effluents, the fractionation of organic compounds in the effluents, and the characterization of the fractions by spectrophotometric methods. The spectral characteristics obtained give some idea about the classes of organic compounds in the effluents and may be useful for studies of the dilution of the effluent in receiving waters.

Determination of abietic acid

A sample of the effluent (usually 500 ml) is acidified and extracted with petroleum ether (3 x 30 ml). The emulsion is broken by centrifugation, the petroleum extracts are combined, and petroleum ether is evaporated in vacuum. The residue is dissolved in chloroform and aliquots (0.2-10 ml) are added to 10 ml of 65 V% sulfuric acid in glass-stoppered 50 ml centrifuge tubes. Chloroform volume is kept constant (10 ml). The tubes are shaken, acetic anhydride (2 ml) is added to each tube and each tube is shaken for 1 min in a cold water bath. The layers are separated by centrifugation, and the spectrum of the sulfuric acid layer is recorded between 550 and 350 nm. The spectrophotometer cells are filled by withdrawing carefully the sulfuric acid layer by a Pasteur pipet and filtering the sulfuric acid solution through a piece of glass wool in a second Pasteur pipet directly into the spectrophotometer cell.

CAUTION - 65 V% SULFURIC ACID IS HIGHLY CORROSIVE. WORK WITH CARE TO PROTECT YOURSELF AND THE SPECTROPHOTOMETER.

Abietic acid has maxima at 519 and 395 nm (Fig. 2). The latter was used for concentration measurements since the absorbance at 519 nm does not increase linearly with concentration (Table 1).

Table 1. Absorbance of abietic acid standard

Abietic acid, mg	<u>Absorbance (1 cm cell)</u>		<u>Absorbance/mg</u>		<u>A519/A395</u>
	<u>519 nm</u>	<u>395 nm</u>	<u>519 nm</u>	<u>395 nm</u>	
0.5	0.154	0.124	0.308	0.248	1.24
1.0	0.295	0.234	0.295	0.234	1.21
1.5	0.508	0.369	0.338	0.246	1.38
2.0	0.750	0.502	0.375	0.251	1.49
			Mean	0.245	

From the data in Table 1, concentration of abietic acid $C = 4.08 A_{395}$. The data serve only as an example and the calibration should be carried out frequently. The standard solutions of abietic acid change on standing and a new solution should be prepared every 3 days. The change occurring in the standard solution is apparent from the spectrum: the maximum at 395 nm increases, eventually becomes higher than the maximum at 519 nm, ($A_{519}/A_{395} = 0.043$), and the relationship between abietic acid concentration and absorbance at 395 nm changes to $C = 3.48 A_{395}$. The reason for the change of the abietic acid standard is not clear at the moment. Abietic acid was recovered from an aged solution by evaporation of chloroform in vacuum and IR spectrum of the residue was recorded. A new absorption bond was observed at 770 cm^{-1} .

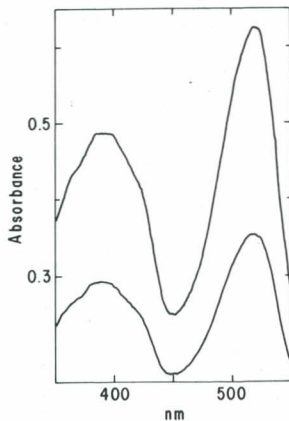


Fig. 2. Spectrum of the reaction mixture: abietic acid - acetic anhydride - sulfuric acid; 1 and 2 mg of abietic acid in the mixture.

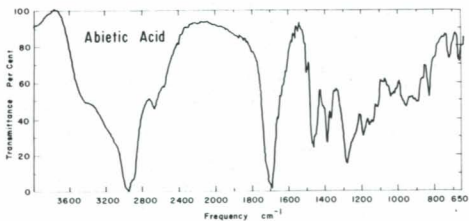


Fig. 3. IR spectrum of abietic acid. KBr pellet.

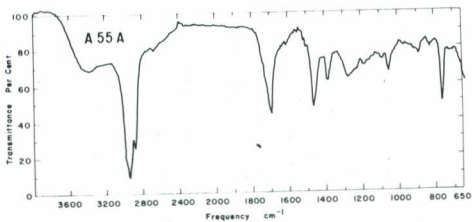


Fig. 4. IR spectrum of the petroleum ether extract of the sulfate clarifier effluent. Neat.

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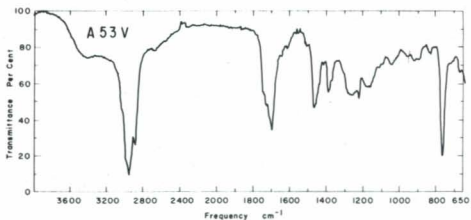


Fig. 5. IR spectrum of the petroleum ether extract of the groundwood mill effluent. Neat.

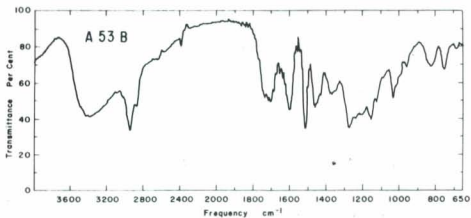


Fig. 6. IR spectrum of the ther extract of the groundwood mill effluent. KBr pellet.

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extracted in a Soxhlet extractor for 24 hours with chloroform. The chloroform solution was dried with anhydrous sodium sulfate and chloroform was evaporated in vacuum to yield the carbon-chloroform extract (CCE). Residual chloroform was left to evaporate from the activated carbon overnight and the carbon was extracted with ethanol in a Soxhlet extractor for another 24 hours. Ethanol was evaporated in vacuum to yield the carbon-ethanol extract (CEE).

IR spectra of CCE (Fig. 7) display essentially the same features as IR spectra of ether extracts and have more pronounced alcoholic carbon-oxygen stretching bands than ether extracts. The latter are always the most intensive bands in CCE isolated from sulfate mill effluents. Carbonyl band at 1730 cm^{-1} is more intensive in CCE isolated from foams than in CCE isolated from effluents, and in many cases it is the most intensive band in IR spectra of foam CCE.

Aeration of the debarker effluent intensifies all carbon-oxygen bands in IR spectra of CCE (Fig. 8). IR spectrum of CCE from the aerated effluent also contains absorption maxima at 765 and 795 cm^{-1} , characteristic for lignins, and indicating that even lignins are at least partly degraded and the degradation products appear in CCE. (Undegraded lignin collects as an interphase on extraction of effluents or condensed foams with petroleum ether and ether).

While IR spectra of petroleum ether and ether extracts from sulfate and groundwood mill effluents are basically very similar, IR spectrum of groundwood CCE differs very much from that of a sulfate effluent (Fig. 9). Groundwood CCE contains very pronounced peaks indicating aromatic structures (3040 , 1610 , 1520 , and $760\text{--}780\text{ cm}^{-1}$). Aliphatic (1715 cm^{-1}) and aromatic (1680 cm^{-1}) carbonyls are present. The somewhat unusual band at 1770 cm^{-1} may indicate the presence of a γ -lactone, or a phenolic ester. α -halogenated ketones also absorb strongly in this region, but their presence in this fraction is unlikely. The band at 1225 cm^{-1} supports the phenolic ester assignment.

IR spectra of CEE indicate that CEE contain more polar compounds than CCE. The carbonyl band at 1730 cm^{-1} is very prominent in the clarifier effluent and foams CEE and the spectrum contains a characteristic sharp peak at 1390 cm^{-1} (Fig. 10). CEE of debarker effluent contains characteristic strong bands at 935 and 800 cm^{-1} , and very strong bands at 1020 , 1070 , and 1250 cm^{-1} (primary and secondary alcohols and phenols

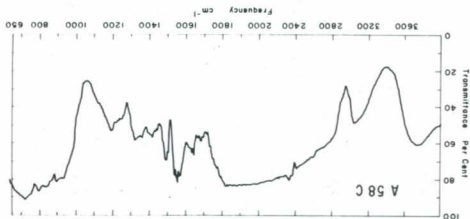


Fig. 7. IR spectrum of CCE of the sulfate debarker effluent. KBr pellet.

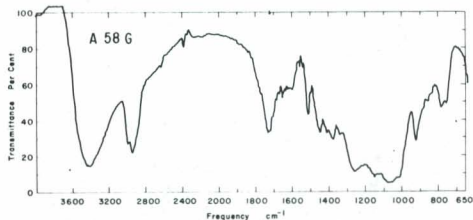
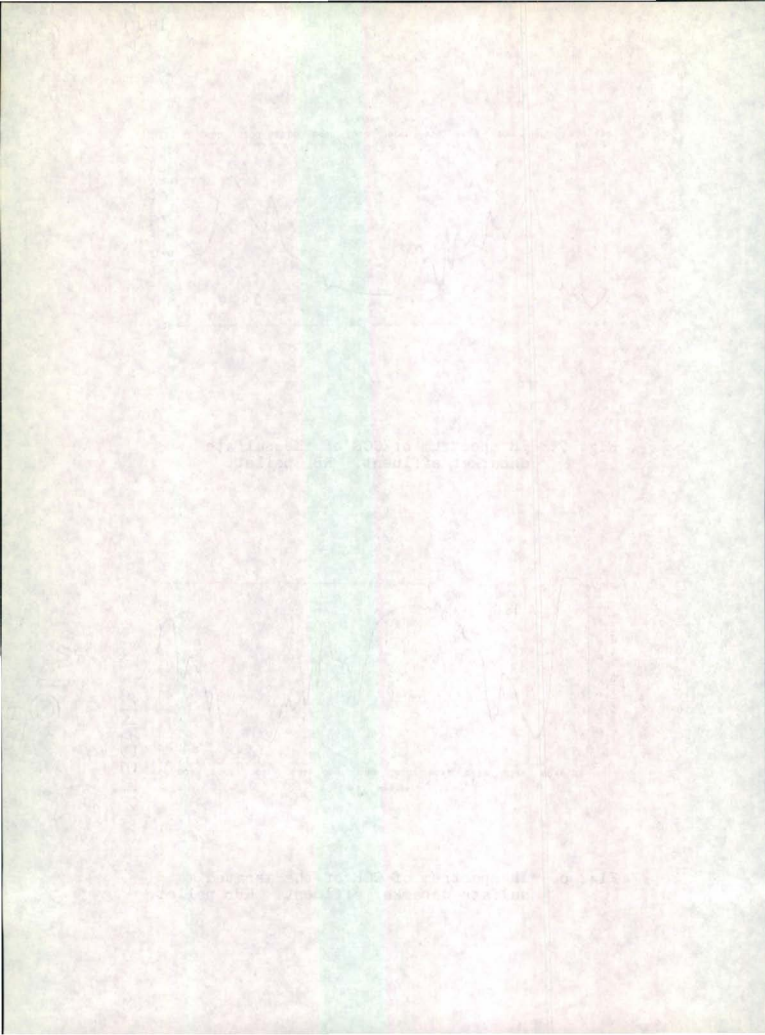


Fig. 8. IR spectrum of CCE of the aerated sulfate debarker effluent. KBr pellet.



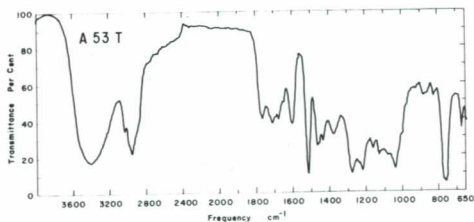


Fig. 9. IR spectrum of groundwood CCE. Neat.

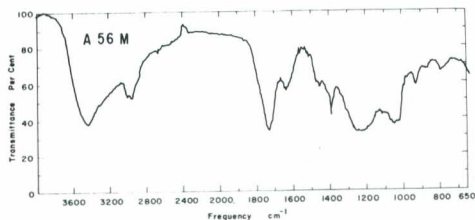


Fig. 10. IR spectrum of CEE of the sulfate clarifier foam. KBr pellet.

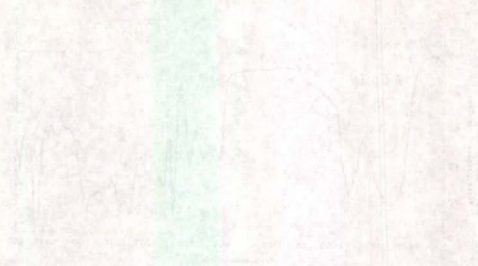


Figure 1. Comparison of the two signals.

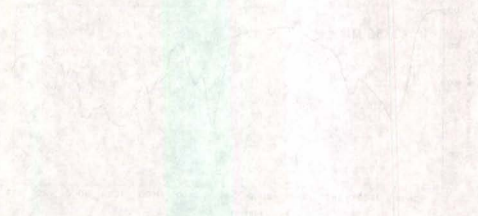


Figure 2. Comparison of the two signals.

Fig. 11).

Similar to the groundwood CCE, IR spectrum of groundwood CEE contains clearly pronounced aromatic patterns. On the other hand, only aromatic carbonyls (1670 cm^{-1}) are present in the latter (Fig. 12).

An interphase is formed during the extraction of acidified effluents or condensed foams with petroleum ether and ether. The interphase can be separated and concentrated by centrifugation, and isolated as dark solids by drying in vacuum (30 psi) at 35°C . A characteristic IR spectrum of an interphase isolated from sulfate or groundwood effluent is presented in Fig. 13. Absorption bands at 860 and 900 cm^{-1} indicate the presence of lignin. These bands are absent from otherwise similar spectrum of an interphase isolated from debarker effluent (Fig. 14). The latter spectrum indicates an acidic polysaccharide, although the band at 1520 cm^{-1} shows the presence of benzene rings. Polysaccharides may also be present in the former preparation. It has been shown previously (57) that macromolecular compounds such as humic acids and lignosulfonates are collected in the interphase on extraction of aqueous solution with an organic solvent.

Concentrations of the fractions, obtained as described above, in various effluents and foams, are presented in Table 2. The data indicate that the debarker effluent is the main source of resin acids. Other effluent streams may contain additional resin acids, but due to the large volume of these effluents, the final concentration of resin acids in the clarifier effluent is much lower than the concentration in the debarker effluent alone. Aeration of the debarker effluent causes a decrease in the concentration of the less-polar fractions (petroleum ether extract, resin acids). The Acadia effluent contains all fractions in much higher concentration than the Fraser's clarifier effluent and it is not surprising that its $\text{LT}_{50} = 2.8\text{ h}$ (at 65%, Atlantic salmon parr) and that it remains toxic even when diluted to 2-5% (58). All fractions are also more concentrated in the foams than in the effluents which is in agreement with the qualitative observation (46).

In the case of the groundwood mill effluent, the aqueous solution after the ether extraction was concentrated in vacuum and dialysed against distilled water. The dialysate was treated with activated carbon to isolate CCE and CEE as described. The nondialysable fraction was treated with 2 volumes of ethanol to yield a precipitate, 230 mg/l (expressed in terms of the original effluent). The supernatant was evaporated to dryness yielding a residue, 29 mg/l . According to its IR spectrum, the precipitate was an acidic polysaccharide. IR spectrum of the supernatant residue indicated the presence of lignin.

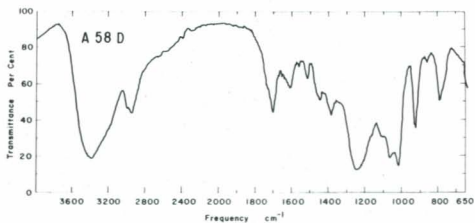


Fig. 11. IR spectrum of CEE of the sulfate debarker effluent. KBr pellet.

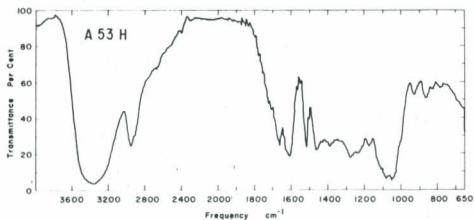
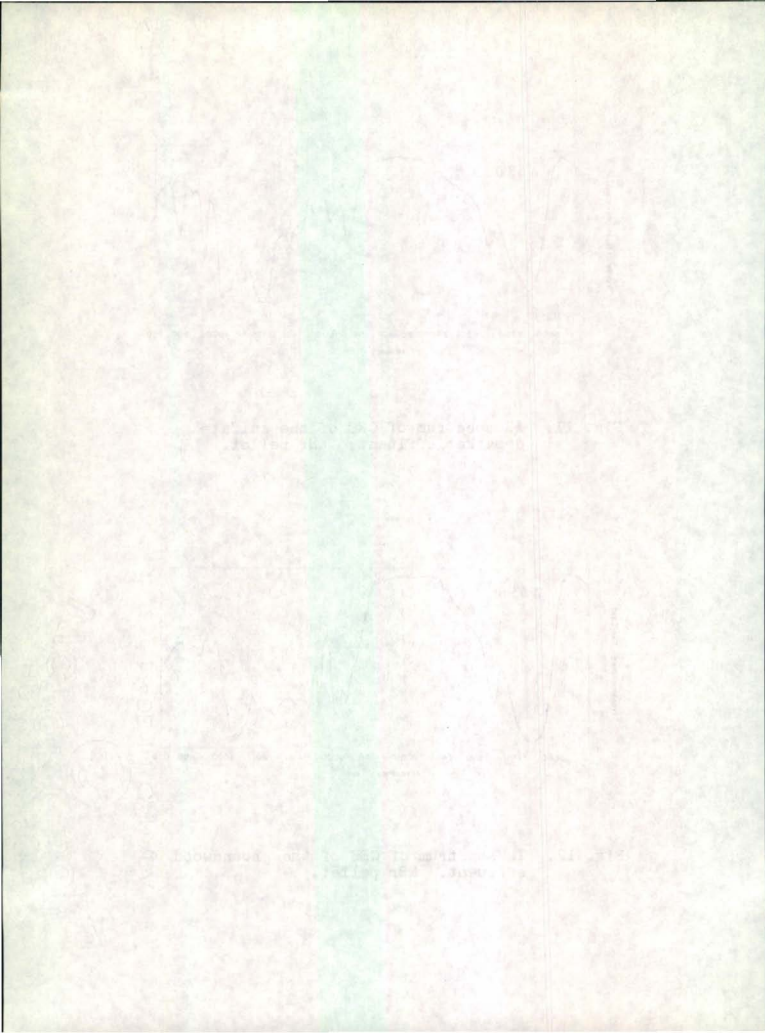


Fig. 12. IR spectrum of CEE of the groundwood effluent. KBr pellet.



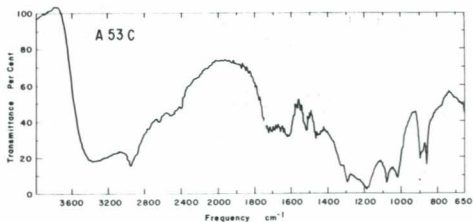


Fig. 13. IR spectrum of groundwood petroleum ether interphase. KBr pellet.

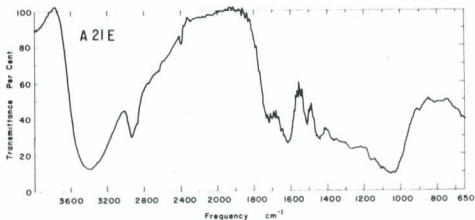


Fig. 14. IR spectrum of sulfate debarker petroleum ether interphase. KBr pellet.

1. The first part of the report is a general introduction to the subject of the study. It discusses the importance of the study and the objectives of the research.

2. The second part of the report is a detailed description of the methodology used in the study. It includes information about the sample, the data collection methods, and the statistical analysis.

3. The third part of the report is a discussion of the results of the study. It presents the findings of the research and discusses their implications for the field of study.

4. The fourth part of the report is a conclusion and a list of references. The conclusion summarizes the main findings of the study, and the references list the sources of information used in the research.

Table 2. Concentration of organic compounds in effluents and foams.

Sample	Concentration, mg/l. in the original effluent				
	Petroleum ether extract	Resin acids as Abietic acid	Ether extract	CCE	CCE
Debarker effluent August 22, 1969	180**	180	**	17	19
Debarker effluent December 19, 1969	173	108	70	44	60
Debarker effluent December 19, 1969 (aerated for 14 days)	57	62	56	54	53
Clarifier effluent August 22, 1969	30**	21	**	11	14
Clarifier effluent October 21-22, 1969	28	23	39	not determined	not determined
Total effluent* October 21, 1969	93	34	82	23	76
Foam, before bypass December 8, 1969	140	127	105	16	62
Foam, after bypass December 8, 1969	49	33	41	33	72
Foam, boom November 19, 1969	57	28	132	11	30
Foam, clarifier November 15, 1969	65	53	46	10	57
Foam, sluiceway November 21, 1969	97	58	96	9	41

All samples are from the Fraser's pulp mill at Newcastle, N.B., except for total effluent* collected from the Acadia pulp mill at South Nelson, N.B.

The samples were taken by Dr. R. H. Cook, RDB, Halifax, N.S., and by the New Brunswick Water Authority.

**The sample was extracted with ether.

Fiber, removed from the groundwood mill effluent by filtration through cheese cloth and glass wool, 10 g/l, was air-dried and extracted with petroleum ether, chloroform, and ethanol, yielding 280, 212, and 475 mg/l of the extracts respectively. The petroleum ether fraction contained 182 mg/l of resin acids expressed as abietic acid.

During the negotiations between RDB and the management of the Fraser's pulp mill on pollution abatement measures, removal of fiber from the effluent, used for fish bioassay, by filtration was questioned and it was suggested that some other dissolved or suspended organic matter may also be removed. Three used filters were delivered to St. Andrews for analysis. The filters were extracted with acidified methanol, the extract was diluted with water and extracted with ether to yield ether extract, 292 mg, and an interphase, 60 mg. The ether soluble material was divided into strong acid, weak acid, and neutral fractions by extraction with 0.6M sodium bicarbonate and 1M sodium hydroxide, both in 10% sodium chloride, to yield 15, 32, and 172 mg of the respective fractions. The IR spectra of the strong and weak acid fraction were similar to that of the ether extract of the effluent. The spectrum of the neutral fraction indicated that this fraction actually contained organic acids not soluble in aqueous alkali, but forming sodium salts soluble in ether. IR spectrum of the "neutral" fraction contained a carboxylate band at 1570 cm^{-1} and could be converted by shaking with diluted hydrochloric acid into the acid form having the carboxyl band at 1710 cm^{-1} .

The strong and weak acid fractions indicated that some organic matter was removed from the effluent by filtration. The origin of the "neutral" fraction is not clear. One possible source may be the filter material.

Preliminary toxicity tests with small Atlantic salmon parr (1 fish per 2 l of solution in a 3-l Erlenmeyer flask) indicate that the toxicity of the fractions decreases with their increasing polarity (Table 3). In spite of their preliminary character, the data suggest that the petroleum ether extract from the debarker effluent may contain other toxic compounds in addition to resin acids.

Characterization of organic compounds in the effluents by UV spectrophotometry

UV spectrum of the sulfate mill (Fraser's) effluent shows a steady increase of absorbance with decreasing wavelength. The difference spectrum (57) has a maximum at 248 nm and a minimum of 280 nm which indicates the presence of a small amount of lignin-type material. UV spectrum of the groundwood mill (Acadia) effluent has maxima at 320 and 283 nm. The difference spectrum has maxima at 356, 295, and 249 nm. The

Table 3. Preliminary data on the toxicity of the fractions of organic compounds from the effluents to Atlantic salmon parr.

Fraction or Compound	Concentration mg/l	Time to death, hours
Petroleum ether extract, debarker effluent	10.3	<1
Petroleum ether extract, foam before woodroom bypass	12.7	8
Petroleum ether extract, foam after woodroom bypass	11.8	31
Ether extract, debarker effluent	10.2	no mortality 142 h
CCE, debarker effluent	10.7	no mortality 94 h
CEE, debarker effluent	9.8	no mortality 94 h
CCE, foam, before woodroom bypass	7.0	no mortality 144 h
CEE, foam, before woodroom bypass	13.8	no mortality 144 h
Abietic acid	10.5	21
Dehydroabietic acid	9.5	13
Crude tall oil	10.6	13
Technical pinene	10.6	no mortality 94 h

maxima at 295 and 249 nm are characteristic of lignin and are also present in the spectrum of sulfite pulp mill effluents (57). The maximum at 320 nm in the normal and 356 nm in the difference spectrum is probably due to the presence of syringaldehyde, acetovanillone, and phenylcoumarone structures (30,32) and may be characteristic of groundwood mill effluent (Fig. 15).

UV spectral characteristics of fractions isolated from sulfate and groundwood mill effluents are summarized in Table 4.

Maxima at about 250 and 290-300 nm in the difference spectra may be assigned to many lignin-type phenolic structures (30).

Judging from the absorbance values, the highest concentration of lignin occurs in CCE of the groundwood mill effluent. Lignin in the macromolecular (nondialysable fraction) is different from that in the other fractions since its difference spectrum does not have a maximum at 340-350 nm. Lignin compounds in the sulfate mill effluents fractions are

Table 4. UV spectral characteristics of fractions isolated from sulfate and groundwood mill effluents.

Maxima (M) and minima (m) absorbance, $1 \text{ cm}^{-1} \text{ mg}^{-1}$, and (wavelength, nm)

Fraction	Normal Spectrum		Difference Spectrum			
	Groundwood mill effluent					
Ether extract	1.49(323)	1.49(288)	M 0.61(355)	0.23(297)	2.66(252)	
			m -0.57(320)	-0.28(280)	-0.26(235)	
CCE	4.68(308)	12.85(281)	M 3.80(348)	7.05(301)	29.5(250)	
			m -1.29(321)	-5.85(278)	-1.31(235)	
CEE		8.57(281)	M 0.52(341)	5.52(301)	12.9(249)	
			m 0.17(328)	0.35(278)	5.98(234)	
Nondialysable fraction, precipitate*			M 0.29(297)	0.51(252)		
Nondialysable fraction, supernatant**	1.12(325)	2.75(281)	M 2.24(300)	3.41(251)		
			m 1.29(280)	5.40(238)		
Fiber, chloroform extract***	5.32(311)	8.68(283)	M (343)	(298)	(253)	
			m (320)	(275)	(235)	
Fiber, ethanol extract		7.70(283)	M 0.20(342)	1.12(298)	2.55(253)	
			m -1.32(320)	-1.07(278)	-3.20(235)	
<u>Sulfate mill effluent</u>						
Ether extract			M 1.34(348)	0.48(298)	0.22(255)	
			m -0.48(316)	-0.80(271)	-3.46(236)	
Filtered-off material, strong acid fraction		12.9(280)	M 1.83(340)	-0.34(301)	-2.93(258)	
			m -1.31(318)	-3.51(270)	-9.08(238)	
Filtered-off material, weak acid fraction		11.3(275)	M 5.78(342)	3.70(305)	5.45(251)	
			m 2.78(316)	-2.49(276)	-5.35(233)	

Solvent: ethanol

*water

**50% aqueous ethanol

***Because of turbidity in the acidified portion, quantitative data could not be obtained for the difference spectrum.

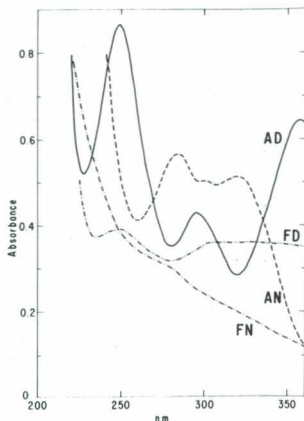


Fig. 15. UV spectra of sulfate and groundwood mill effluents (1 cm cells, 5 ml of effluent diluted to 100 ml with distilled water, baseline for difference spectra at absorbance = 0.3).

FN, AN = normal spectrum of sulfate and groundwood effluent resp.

FD, AD = difference spectrum of sulfate and groundwood effluent resp.

also quite different from those in the groundwood mill effluents.

Groundwood mill effluent fractions were characterized, in addition, by their fluorescence excitation and emission spectra. The data are presented in Table 5.

Table 5. Fluorescence spectra of fractions from the groundwood mill effluent.

Fraction	Excitation maximum, nm	Emission maximum, nm
Ether extract	320	384
Nondialysable fraction, precipitate	no significant fluorescence	
Nondialysable fraction, supernatant	270	330 356 380
CCE	284	318
CEE	290 336	312 412
Fiber, chloroform extract	285 320	320 364
Fiber, ethanol extract	330	380

Conclusions

The report provides quantitative data on the levels of resin acids and several fractions of organic compounds in sulfate and groundwood mill effluents.

The analytical techniques for the determination of resin acids should be improved. A method based on the separation and measurement of resin acids by gas chromatography may be the best choice.

According to the general characterization of the other organic compounds by UV and IR spectrophotometry, functional groups present are mainly aliphatic and aromatic hydroxyls, carbonyls, and carboxyls.

Compounds toxic to fish are present in the less-polar fractions. These compounds should be identified and quantitative methods should be developed to study their concentration in

receiving waters and their fate in different waste-treatment processes. More general parameters such as COD or TOC could be used to measure the total of other organic compounds. UV spectrophotometry may be used to measure the concentration of the effluents in receiving waters.

Contrary to general beliefs, the groundwood effluent carries a high load of organic compounds and should be subjected to not only primary but also to secondary treatment.

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