THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

EVALUATION OF ANALYTICAL PROCEDURES FOR THE ANALYSIS OF KRAFT EFFLUENTS

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Report One

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SUMMARY

A method for the determination of oleic, linoleic, isopimaric, and abietic acids in kraft effluents was established. Also, a procedure for the measurement of α and β-pinene and dimethyl disulfide was developed. Dimethyl sulfide was not quantitatively extractable with organic solvents and therefore was not determinable by the procedure for pinenes and sulfides.

The fatty and resin acids were extracted from the acidified effluent with ethyl ether, methylated, and separated by gas chromatography. An internal standard was used to convert the areas of the peaks to absolute values.

The pinenes and sulfides were extracted from an acidified, salt-saturated effluent with hexane. The separation was accomplished by gas chromatography. An internal standard was employed for computation.

The two methods were written in laboratory procedure form and are included at the end of this report.

Effluent samples, spiked and unspiked, were analyzed for fatty and resin acids. The recovery and precision of the method was found to fulfill the requirements of the proposal. The sensitivity was found to be greater than requested.

The determination of the pinenes was satisfactory in respect to recovery, precision, and sensitivity. The method lacks the necessary sensitivity to dimethyl disulfide which tends to influence the precision. The recovery of dimethyl disulfide was fair.

The total working time was found to be within the three-hour proposal when multiple samples were analyzed. The method for the neutral components is very simple and requires very little time. The preparation of the diazomethane for the methylation of the acids was found to be time consuming but if a number of samples are being run simultaneously, the preparation represents a small fraction of total analysis time per sample.

INTRODUCTION

This project was undertaken as an evaluation of currently used extraction procedures and chromatographic techniques for the determination of selected compounds in kraft mill effluents. The primary objective was the development of a procedure that would detect as little as 0.05 milligram per liter of these compounds in the 0-1 milligram per liter range with a precision of $\pm$ 0.025 milligram per liter. The procedure was to be suitable for semiroutine analysis with a total working time of less than three hours.

The selected compounds were as follows:

Oleic acid
Linoleic acid
Isopimaric acid
Abietic acid
α-Pinene
β-Pinene
Dimethyl disulfide
Dimethyl sulfide

EXPERIMENTAL APPROACH

The eight compounds were divided into three groups as far as extractability and chromatography procedures are concerned. The three groups are: acidic material, terpenes, and neutral sulfides. Previous work in our laboratory required the determination of acidic materials and terpenes but very little if any work had been done on neutral sulfides. The experience with acidic materials was generally associated with tall oil and liquor analysis. Kraft mill condensates have been frequently analyzed for pinenes and other volatiles such as alcohols. In both cases the concentration of the components in the samples was of a greater magnitude than was to be encountered in this project.

Initially, it was planned to reduce the three groups to two by combining the neutral sulfides with the pinenes. The similarity of the two in respect to solubility and volatility suggested this approach. One chromatographic column that would perform satisfactory separation of the acidic materials as well as neutral compounds was given consideration as a time-saving contribution, but the nature of the two groups made this innovation impractical.

In the proposal, a two-step extraction with an immiscible organic solvent was to be used for the separation of the two groups. The alkaline effluent was to be extracted directly for the separation of the neutrals (sulfides and pinenes), and subsequently acidified for the extraction of the acidic material. Various organic solvents were to be tested for their effectiveness in the removal of the compounds. The extraction of the neutrals must serve two purposes. Besides removing the neutral components, the extraction must serve as a means of providing a more concentrated solution without concentrating by evaporation of

the solvent. It was quite apparent that evaporation of the solvent would result in similar evaporation of the more volatile components of the neutral group.

An internal standard for each group was to be selected. It would serve primarily as a means of computing the absolute amount of each of the components. It would also compensate for any mechanical losses during the steps leading up to the chromatographic analysis.

In the preliminary work, all the samples analyzed would be prepared in the laboratory with various amounts of the components in distilled water. Recovery and sensitivity data were to be gathered from such synthetic samples. Secondly, a sample of kraft mill effluent was to be provided for spiking purposes to determine the recovery of various components.

Finally, six samples of various mill effluents were to be analyzed.

EXPERIMENTAL

ACIDIC GROUP — INTRODUCTION

The analysis of the acids followed a procedure which has been used in our laboratory in the past. Modifications had to be made to compensate for the small quantities that were to be determined.

A column 6 ft. x 1/8 in. containing 8% EGSS-X on Gas Chrom Q 100/120 had previously been found to separate the methyl esters of fatty and rosin acids. The packing material was prepared in our laboratory because it was not commercially available at 8% concentration. The support and stationary phase were purchased from Applied Science Laboratories.

The acids were converted to methyl esters for gas chromatography. Although the free fatty acids can be separated without esterification on a FFAP column, the direct method would not apply to resin acids. Sylation of the acids was considered as another means of preparing volatile derivatives. This was not pursued because it offered no apparent advantage over the methyl esters.

Oleic and linoleic acid were obtained from Applied Science Laboratories and were reported to be 99+% pure by thin layer and gas chromatographic analysis. Pure isopimaric and abietic acid were not commercially available. Naval Stores Laboratory, Olustee, Florida furnished the pure isopimaric acid and levopimaric acid which was used in preparing abietic acid. Abietic acid which is very unstable can be prepared from levopimaric acid by a very simple process described by Schuller, et al. (1). The individual acids used in this work were methylated and analyzed by gas chromatography to determine their purity.

EXTRACTION OF ACIDS

Successive extractions with ethyl ether after acidification appeared to quantitatively remove the acids from the effluent. Initially, a preextraction from an alkaline solution was proposed for the removal of neutrals but a significant amount of acidic material was also extracted along with the neutral material. (Table I).

TABLE I

EFFECT OF PREEXTRACTION ON ACID CONTENT

(Effluent sample)

Acid	Preextract, mg./l.	Direct Extract, mg./l.
Oleic	0.39	1.80
	0.14	1.79
Linoleic	0.01	0.0096
	0.01	0.0024
Isopimaric	1.30	1.77
	1.12	1.70
Abietic	0.22	0.31
	0.19	0.30
Dehydroabietic	2.65	3.15
	1.74	3.04

A quantitative extraction was accomplished by acidifying a 100-ml. sample to a pH of about 4 using dilute sulfuric acid and Congo red paper, prior to the extraction with ethyl ether. Three portions of ether (25, 15, and 10 ml.) were used successively. The ether fractions were placed in a second separatory funnel and finally washed with about 10 ml. of water that had been acidified. The ether fraction was evaporated to dryness on a vacuum rotary evaporator and immediately dissolved in about 5 ml. of ether-methanol (9:1).

PREPARATION OF METHYL ESTERS

The methyl esters were formed with diazomethane prepared from Diazald. The Aldrich Chemical Co. method for the preparation of the diazomethane was used for the preparation of an alcohol-free ether solution of diazomethane. The apparatus consists of a 50-ml. distilling flask with a long side arm (50-60 cm.) bent at a right angle at the tip. The tip was drawn to a small orifice to effect the emission of smaller bubbles. Carbitol (3.5 ml.), 37.5% potassium hydroxide (1.2 ml.) and ethyl ether (1.0 ml.) were placed in the flask. A dropping funnel containing 2.2 g. of Diazald in 15 ml. of ethyl ether is placed on top of the flask. The diazomethane is absorbed in 15 ml. of ether by positioning the tip of the side arm below the surface of the ether. A 50-ml. Erlenmeyer flask immersed in an ice bath was used to collect the reaction products. The distilling flask is placed in a water bath (60-70°C.) and the Diazald solution was added over a two-minute period. The dropping funnel was rinsed with about 5 ml. of ethyl ether. The yellow-orange color of the distillate indicates the presence of diazomethane.

Diazomethane was added dropwise to the solutions of free acids until a yellow color persisted. The solution was immediately evaporated to dryness on a vacuum rotary evaporator. The residue was dissolved in 0.5 ml. cyclohexane and transferred to a 1/2-dram vial.

INTERNAL STANDARD — ACIDIC GROUP

Margaric acid (C-17:0) was selected as an internal standard for both the fatty and rosin acids. Margaric acid is not commonly found in wood and is commercially available. The acid used in this study was purchased from Aldrich

Chemical Company and was found to be 97.6% pure by gas chromatography. The most significant contaminant was pentadecanoic acid. A correction was made for the purity of the internal standard when calculating the content of the other acids.

The internal standard was added to the effluent as a solution of margaric acid in tetrahydrofuran. The concentration was adjusted so that a 2.0-ml. aliquot would contain about 0.7-0.8 mg. of margaric acid. The relatively large amount of standard was favored because a more accurate peak area could be established due to greater base-line stability at higher attenuations of the gas chromatograph. Also, small peaks that frequently were present having the same retention as margaric acid would not impose any significant error.

GAS CHROMATOGRAPHIC ANALYSIS — ACIDIC GROUP

A Varian model 1520 gas chromatograph and a Honeywell recorder equipped with a Disc integrator were used for the separation and measurement of the acids. The column effluent was monitored with a hydrogen flame ionization detector. Temperature programming was found to be necessary for adequate separation.

A column (6 ft. x 1/8 in. S.S.) containing 8% EGSS-X on Gas Chrom Q 100/120 was conditioned for 48 hours at 220°C.

It was necessary to find a temperature program that would provide adequate separation in a minimum amount of time. The program that had been used in our analyses of tall oils was found to be unacceptable in determining the small amounts in this project. A lower rate of programming had been employed over a longer span of time. At the high sensitivity required for the small quantities involved in the present work, any temperature change caused a significant base-line shift which in turn made the integration of the peak difficult. Therefore,

a program that was isothermal during the elution of the acids was devised. Table II shows the various programs and retention times. A program maintaining a temperature of 175°C. for 25 minutes followed by a rapid increase of 10°/min. to 210°C. appeared to satisfy the requirement of the analysis.

TABLE II

COMPARISON OF COLUMN TEMPERATURES
FOR ACID SEPARATION

Conditions	Retention Time				
	C-17:0	C-18:1	C-18:2	Isopimaric	Abietic
170° for 15 min., 2°/min.-220°C.	11.5	17.5	21.1	41.5	48.7
172° for 25 min., 4°/min.-210°C.	11.4	17.7	22.8	45.6	55.3
172° for 25 min., 6°/min.-220°C.	11.5	17.7	22.7	43.4	51.4
175° for 25 min., 10°/min.-210°C.	10.4	16.1	21.5	42.3	51.2

DETECTOR FACTORS — ACIDIC GROUP

Factors used in the computation of the acids based on an internal standard were determined for each component (Table III).

TABLE III

DETECTOR FACTORS[a]

Compound	Factor
C-18:1	1.00
C-18:2	0.94
Isopimaric	1.04
Abietic	0.98

[a]Detector factor = peak area response/mg. acid divided by peak area response/mg. standard.

A mixture containing known amounts of acids and internal standard was methylated and chromatographed. The peak areas per unit weight were computed for each component. The ratio of the area per milligram values of the acids to the area per milligram of internal standard represent the relative response of each acid to the internal standard. Compounds of similar compositions should give a similar detector response. The values in Table III justify a factor of unity. The minor differences in the factors might reflect the purity of the acids.

Linoleic and abietic acid are very unstable which could account for the slightly lower response factors.

RECOVERY AND PRECISION — ACIDIC GROUP

A sample of a typical kraft mill effluent was used in the study of recovery and precision of the analytical methods. The effluent was analyzed for the acidic materials present (Table IV). The dehydroabietic acid found in the effluent was probably a product of the abietic acid. Although dehydroabietic acid was not originally designated as being of interest in the project, it was concluded that, since this acid originates from abietic acid, it should be quantitatively determined.

Recoveries of added components to the effluent are shown in Table V. The spiking was accomplished by preparing a known mixture of the acids in tetrahydrofuran and adding a measured quantity to the effluent before extraction.

The reproducibility of the method was displayed by analyzing the original effluent sample plus two additional effluents that were received at a later date (Table VI). The later two samples represent a treated and untreated mill effluent.

TABLE IV

ANALYSIS OF EFFLUENT

Peak No.	Retention Time	Identification	Concn., mg./l.
1	2.3	--	--
2	2.8	--	--
3	4.8	C-15:0	--
4	5.7	--	--
5	7.4	C-16:0	--
6	9.3	--	--
7	10.4	C-17:0	--
8	16.1	C-18:1	1.80
9	18.7	--	--
10	21.5	C-18:2	0.006
11	29.3	--	--
12	32.8	--	--
13	36.2	Pimaric (?)	--
14	39.7	Palustric (?)	--
15	42.2	Isopimaric	1.70
16	47.5	--	--
17	51.0	Abietic	0.30
18	54.0	Dehydroabietic	3.10

TABLE V

RECOVERIES OF ADDED ACIDIC COMPOUNDS

(All values = mg./l.)

Acid	Present	Added	Total	Total Found	%
Oleic	?	--	--	1.80	
	?	--	--	1.79	
	1.80	1.08	2.88	2.90	101
	1.80	1.08	2.88	2.72	94
Linoleic	?	--	--	0.0096	
	?	--	--	0.0024	
	0.0060	0.88	0.886	0.92	104
	0.0060	0.88	0.886	0.90	102
Isopimaric	?	--	--	1.77	
	?	--	--	1.70	
	1.74	1.54	3.28	3.10	96
	1.74	1.54	3.28	3.58	110
Abietic	?	--	--	0.31	
	?	--	--	0.30	
	0.30	1.30	1.60	1.48	91
	0.30	1.30	1.60	1.52	94

TABLE VI

DUPLICATE ANALYSIS OF MILL EFFLUENTS (MG./L.)

Sample	Oleic	Linoleic	Isopimaric	Abietic	Dehydroabietic
Original effluent	1.80	0.0096	1.77	0.31	3.15
	1.79	0.0024	1.70	0.30	3.04
Untreated effluent	3.36	0.35	5.64	3.63	4.92
	3.56	0.36	4.86	2.98	4.50
Treated effluent	0.022	<0.01	0.98	0.54	0.43
	0.030	<0.01	0.92	0.51	0.51

The complete analysis of the untreated and treated samples may be found in Table VII. The unidentified peaks do not necessarily represent acid components. The rosin acids were identified by comparing retention times with the retention times of the components of a WW gum rosin from the Naval Stores Laboratory, Olustee, Florida. The laboratory furnished a chromatogram and an analysis of the rosin.

TABLE VII

ACIDIC COMPOSITION OF TREATED AND UNTREATED EFFLUENTS

Peak No.	Identification	Untreated, mg./l.	Treated, mg./l.
1	?	--[a]	--[a]
2	?	1.60	0.11
3	C-16:0	2.10	0.31
4	?	0.96	<0.02
5	C-18:0	0.051	<0.01
6	C-18:1	3.46	0.026
7	C-18:2	0.36	<0.01
8	?	1.55	<0.01
9	?	0.48	0.14
10	?	0.13	<0.01
11	?	0.54	0.14
12	Palustric	1.52	0.14
13	Isopimaric	5.25	0.95
14	?	0.32	0.02
15	Abietic	3.30	0.52
16	Dehydroabietic	4.71	0.47
Total acidic material		26.3	2.8

[a]This peak appeared on the solvent tail and was relatively small. Therefore, no computation was made.

NEUTRAL GROUP — INTRODUCTION

This group includes α- and β-pinene, dimethyl sulfide, and dimethyl disulfide. The pinenes used in this work were purchased from Aldrich Chemical Company. The neutral sulfides were supplied by Eastman Organic Chemicals.

Several columns were to be evaluated as to their ability to separate the four components in this group. The EGSS-X column used in the acid analysis was suggested as only a possibility that could save working time. A 10% Triton X-305 column has been used by others (2) for the separation of the sulfides. A 10 ft. x 1/8 in. column containing 20% Carbowax 1500 had been used successfully in our laboratory for the separation of α- and β-pinene in kraft mill condensates.

The components were to be separated from the effluent by solvent extraction, as proposed, and therefore no other means of separation such as stripping or distillation were evaluated.

GAS CHROMATOGRAPHY — NEUTRAL GROUP

The effluents of the columns were monitored with a flame ionization detector which works satisfactorily for both pinenes and organic sulfides. There would have been an advantage in using an electron capture for the sulfides because sulfur-containing compounds could be detected in much smaller quantities than with a flame detector. The use of two detectors would add to the complexity of the method to the extent that the idea was not given further consideration.

The use of the EGSS-X column was eliminated when a retention time of about one minute was recorded for α-pinene. The column temperature was 50°C.

The Triton X-305 column bled too much at the required temperatures for elution of the pinenes. The background produced could not be bucked out at the high sensitivities required in this analysis.

A mixture of the sulfides and pinenes was separated on a column (10 ft. x 1/8 in.) containing 20% Carbowax 1500. The column was held at 50°C. for five minutes and then programmed to 100°C. at 2°C./min. The retention times were: dimethyl sulfide, 3.7 min.; α-pinene, 9.8 min.; dimethyl disulfide, 11.7 min.; and β-pinene, 12.3 min. To produce a better separation of the dimethyl disulfide from the β-pinene and to provide longer retention time for dimethyl sulfide, a 20 ft. column was packed and conditioned for 48 hours at 150°C. The retention times of the neutrals and the solvent are shown in Table VIII.

TABLE VIII

RETENTION TIME OF NEUTRALS (MIN.)

Temperature	Ether	Me_2S	α-Pinene	Me_2S_2	β-Pinene
65-100°C. at 4°/min.	5.0	7.7	20.7	29.0	31.2
65-100°C. at 2°/min.	5.3	8.7	23.2	31.6	34.0

Note: The use of hexane as a solvent in place of ether necessitated a longer retention time for dimethyl sulfide. Therefore, the column was held at 65° for 5 minutes and programmed to 90°C. at 2°/min.

EXTRACTION OF NEUTRALS

The finding of a good solvent for the extraction of the neutrals was very difficult because of the many requirements that had to be met. It was calculated from the detector response of the sulfides that the maximum amount of solvent that could be used to extract 100 ml. of effluent would be two milliliters.

Ethyl ether, which would have been a good solvent because of its short retention time was eliminated due to its solubility in water. Several solvents were evaluated for their retention times (Table IX).

TABLE IX

RETENTION OF SOLVENTS

Solvent	Time, min.
Hexane (Baker's)	4.6 & 6.0 (2 peaks)
Hexane (M.C.B.)	4.5, 6.0, & 7.2 (3 peaks)
Hexane (Fisher)	4.4 & 5.8 (2 peaks)
Chloroform	8.3
Dichloromethane	10.2, 13.0, & 16.0 (3 peaks)
Isopropyl ether	5.8
Trichloroethylene	20.0
Butyl ether	18.5
Cyclohexane	7.0

Baker's hexane was selected as a solvent even though the second peak was quite close to dimethyl sulfide. Hexane separates well and is almost completely insoluble in water. It was found necessary to check each batch of hexane to make certain that a third peak is not present. It would be advantageous to be able to obtain only the material that gives rise to the first peak and use it as a solvent.

INTERNAL STANDARD

The ideal internal standard would be a compound that would be insoluble in water, soluble in hexane, and have a retention time that would provide a separation from other components of the effluents. Cyclic hydrocarbons of various

molecular weights were evaluated because they usually exhibit only one peak when chromatographed.

Cycloheptane was eluted as a single peak at about 16 minutes. The standard was introduced into procedure by adding a known quantity to the hexane. Exactly 2.0 ml. of this hexane was added to a measured quantity of effluent for extraction of the neutrals.

DETECTOR FACTORS — NEUTRAL GROUP

Weighed amounts of the neutral compounds and cycloheptane in hexane were chromatographed to determine the detector factors (Table X).

TABLE X

RETENTION TIMES AND DETECTOR FACTORS

Compound	Retention Time	Detector Factor[a]
Dimethyl sulfide	9.7	0.595
Cycloheptane	15.7	--
α-Pinene	27.0	0.847
Dimethyl disulfide	37.0	0.328
β-Pinene	39.7	0.696

[a]Detector factor = peak area response/mg. of compound divided by peak area response/mg. of internal standard.

The low response for the sulfides was expected because of the high sulfur content but the low response for the pinenes is not understood. The purity of the pinenes would have to be questioned because the carbon-to-hydrogen ratios of the standard and the pinenes is so similar that a response factor of

unity would be expected. No attempts were made to purify the material because for spiking purposes, the response factor will compensate for the purity of the components. But for the determination of absolute values of an unknown effluent it would be necessary to verify the purity of component before a factor was applied.

RECOVERY AND PRECISION — NEUTRAL GROUP

A solution containing known amounts of the neutrals in alcohol was prepared. An aliquot was added to 100 ml. of an analyzed effluent sample and extracted with 2.0 ml. of hexane containing the internal standard. The extract was chromatographed and the amount recovered reported in Table XI.

TABLE XI

RECOVERY OF NEUTRALS

Component	Mg. Added	Mg. Found	Recovery, %
Me_2S	1.16	0.12	10
α-Pinene	0.92	0.95	103
Me_2S_2	0.92	0.68	74
β-Pinene	1.10	1.11	101

The incomplete extraction of the sulfides was probably due to their solubility in water. To reduce the solubility, sodium chloride was added to the aqueous sample at various levels and recoveries were determined for the neutrals. Distilled water was used in place of the effluent for the data reported in Table XII.

The salting of the solution before extraction makes the recovery of dimethyl disulfide complete. The recovery of dimethyl sulfide was increased as the salt concentration increased but a suitable quantitative extraction could not

be obtained. The optimum conditions for extraction would appear to be 100 ml. of acidified effluent plus 25 g. of sodium chloride.

TABLE XII

EFFECT OF SALTING ON RECOVERIES

Conditions[a]	Recovery, %			
	Me_2S	α-Pinene	Me_2S_2	β-Pinene
100 ml. H_2O	12	97	78	100
100 ml. H_2O + 10 g. NaCl	21	106	95	97
100 ml. H_2O + 20 g. NaCl	43	104	103	95
100 ml. H_2O + 25 g. NaCl	51	96	93	98
100 ml. H_2O + 30 g. NaCl	45	103	86	100
100 ml. H_2O saturated with NaCl	46	98	86	92

[a]The concentration of neutrals used in the above study was about 1 mg./l.

An absolute amount of dimethyl sulfide was retained by the aqueous phase rather than a percentage of the amount added. This was displayed by adding about 0.5 mg./l. to water and extracting under the optimum conditions. There was no dimethyl sulfide recovered at this concentration. It would appear that the water will retain a concentration of about 0.5 mg./l.

Carbon tetrachloride was used as a solvent at the 0.5 mg./l. concentration but it also did not extract any dimethyl sulfide.

The three effluents were analyzed for neutrals (Table XIII).

TABLE XIII

EFFLUENT ANALYSIS

Sample	Me_2S, mg./l.	α-Pinene, mg./l.	Me_2S_2, mg./l.	β-Pinene, mg./l.
Typical	None	None	None	None
Untreated effluent	None	0.086 0.077 0.048	0.44 0.54 0.46	0.038 0.042 0.045
Treated effluent	None	None	None	None

The treated effluent was spiked with known amounts of neutrals in the 0.5 mg./l. range. Average recoveries were none for dimethyl sulfide, 92% for α-pinene, 101% for dimethyl disulfide, and 95% for β-pinene.

CONCLUSIONS

A method for the determination of the fatty and resin acids was perfected to the point of satisfying the requirements proposed in the project. The sensitivity of the method exceeds the proposed detectable amount of 0.05 mg./l. by a factor of about 10. The acids recovered after spiking were in the range of 95-100%. A standard deviation for each acid was not established due to the limitations of time for the project. The data from replicate analyses of various effluents would suggest a good reproducibility.

The presence of resin acids in addition to the two suggested in the proposal expanded the scope of the project. Dehydroabietic acid was found to be more prominent than abietic in effluents. Values were established for this acid in addition to several other acids found in the samples.

The determination of the pinenes and sulfides was hampered by the inability to obtain complete extraction of dimethyl sulfide. Good recoveries were achieved for the pinenes and dimethyl disulfides. The detectable limits found for the pinenes would correspond to the amounts proposed, but the weak response of dimethyl disulfide to a hydrogen flame detector made it much less sensitive. The inability to concentrate the extract due to the volatility of the components makes it difficult to increase the sensitivity of the method. The low concentration of the components in the extract required running the gas chromatograph at peak senstivity which is undesirable in respect to maintaining the stable base necessary for good area measurements. Recently purchased gas chromatographs which are solid state and use a flame detector with greater sensitivity would certainly have been an asset in increasing the sensitivity and reproducibility of the method.

The determination of dimethyl sulfide was not accomplished by a liquid-liquid extraction technique. A method of stripping or distillation would seem to be more desirable but would also be more complicated. Chemical modifications of the dimethyl sulfide to produce an extractable compound may be possible. A stripping technique that would remove both the sulfides and pinenes would be worth consideration. The increased quantities that could be introduced into the gas chromatograph by a stripping technique would be an advantage in the precision of the measurement.

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APPENDIX

PROPOSED METHOD FOR FATTY AND ROSIN ACIDS

Extraction: Acidify a 100 ml. sample of effluent with 1N sulfuric acid (Congo red paper). Add an aliquot of a margaric acid solution containing a known amount of acid (0.7 to 0.8 mg.) in tetrahydrofuran. Extract with 3 portions of ethyl ether (25, 15, 10 ml.). Wash the combined ether fractions once with water. Evaporate to dryness on a vacuum rotary evaporator. Dissolve the residue in about 5 ml. of ether-methanol (9:1).

PREPARATION OF METHYL ESTERS

The methyl esters are formed with diazomethane which is prepared as follows: Add 3.5 ml. of Carbitol, 1.2 ml. potassium hydroxide 37.5%, and 1 ml. of ethyl ether to a 50-ml. distillation flask having a long side arm. The tip of the arm is placed below the surface of 15 ml. of ethyl ether contained in a 50-ml. Erlenmeyer flask. The receiving flask is kept in an ice bath. Connect a dropping funnel to the distilling flask and fill 15 ml. of an ether solution containing 2.2 g. of Diazald.

Place the flask in a 60-70°C. bath and add the Diazald solution over a two-minute period. Five milliliters of ether are used to rinse the separate funnel into the flask.

The diazomethane in the receiver is added dropwise to the ether extracts until a yellow color persists. The extract is again evaporated on the rotary evaporator and the residue is dissolved in about 0.5-ml. cyclohexane

and transferred to a 1/2-dram vial for chromatography. This may be evaporated with nitrogen to 0.1 for greater sensitivity.

GAS CHROMATOGRAPHIC ANALYSIS

Conditions:

Column: 6 ft. x 1/8 in. S.S. containing 8% EGSS-X (Applied Science Lab.) on Gas Chrom Q 100/120.

Temperature: 173-175° for 25 minutes ÷ 10°C./min. to 210°C.

Carrier: He — 30 cc./min.

Injector Temperature = 200°C.

Detector Temperature = 235°C.

Detection — H_2 flame

Area Measurements — Disc integrator

Volumn Injected = 2 µl.

Calculation: $$\frac{\text{Area of acid x mg. int. std. x 1000}}{\text{Area of internal std. x ml. of sample}} = \text{mg./l.}$$

PROPOSED METHOD FOR PINENES AND SULFIDES

Acidify 100 ml. of effluent to pH of 4 with 1N sulfuric acid. Add 25 g. of sodium chloride and shake to dissolve. Add 2.0 ml. of hexane that contains a weighed amount of cycloheptane (ca. 4 mg./ml.). Shake for about 20 seconds. Allow 5-10 minutes for the layers to separate. Drain off the aqueous layer. Drain the hexane into a 15-ml. centrifuge tube. Spin the tube for a minute to separate the water from the hexane.

Inject 5 µl. for G.L.C. analysis.

G.L.C. CONDITIONS

Column — 19 ft. x 1/8 in., 20% Carbowax 1500 on Gas Chrom Q 100/120.

Column Temperature — 65°C. for 5 minutes — program to 90°C. at 2°/min.

Injector — 150°C.

Detector — 195°C.

Carrier Gas — He at 30 cc./min.

Detector — H_2 flame

Area Measurement — Disc integrator

Volumn Injected — 5 µl.

Calculation: $$\frac{\text{Area component x mg. of standard x 1000}}{\text{Area internal std. x ml. of sample x detector factor}} = \text{mg./l.}$$