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Gas chromatographic-mass spectrometric analysis of pyrolytic oil distillates

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GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSIS OF PYROLYTIC OIL DISTILLATES

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ABSTRACT

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GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSIS OF PYROLYTIC OIL DISTILLATES

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A sample of pyrolytic oil (condenser oil - project B-469) was vacuum distilled at 50°C/14.5mm - 188°C/19.0mm.

The distillate (25-1) was studied by gas chromatography to establish optimum conditions and apparatus performance for the separation of the components of the distillate. This was achieved by using a 6' x ¼" SE-30 column.

The peaks were identified by using a combined gas chromatographic and mass spectrometric technique. The identification of peaks was also aided by noting enhancement of peak size when known materials were chromatographed with the mixture.

After the components of the mixture were known, a quantitative gas chromatographic analysis procedure was developed.

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INTRODUCTION

The utilization of waste materials is of vital concern in the United States because these materials (forestry, agricultural and municipal wastes) represent unused resources and, in many cases, present serious disposal problems. During the past several years, a great deal of attention has been given to pyrolysis as a means of converting these materials into useful products, particularly fuels.

The total organic material from agricultural crops and food wastes has been estimated at 55,000,000 tons per year. The waste from wood manufacturing residues has been estimated at 56,000,000 tons per year.[1] One ton of organic material is the energy equivalent of one barrel of crude oil.[2] The successful development of an economically feasible method of pyrolyzing these wastes would benefit industrial firms and the people of the United States. The economy would be significantly improved if the pyrolytic oils could be utilized as sources of fuels and/or valuable chemicals.

Workers at the Engineering Experiment Station at the Georgia Institute of Technology have shown that pyrolysis is readily utilized for the conversion of cellulosic and lignocellulosic wastes into useful fuels and products.[3]

The use of pyrolytic oils as fuels is hampered by increasing viscosities of the oils on standing. The

successful stabilization of the pyrolytic oils would thus require a knowledge of the major components of the pyrolytic oils. There have been reports on the pyrolysis products of wood, and it is fairly well established that the pyrolytic oils obtained from the pyrolysis of lignocellulosic materials are composed of low molecular weight aldehydes, ketones, alcohols, aliphatic acids, phenols and other aromatic compounds.[4] The precise composition of the pyrolytic oils obtained from pine sawdust and bark has not yet been established. This study involves the identification of the volatile components of the pyrolytic oils using the combined gas chromatographic-mass spectrometric technique.

Instrumentation

The Combined Gas Chromatograph and Mass Spectrometer.--Gas chromatography is an excellent tool for the separation, detection and quantitation of a complex mixture. It is not a good tool for qualitative identification. The retention time can always be used to deny the possible existence of a compound in an unknown mixture, but the accuracy of retention measurements is not sufficient to eliminate the many thousands of compounds that might elute within the observed time period. The methods available to obtain different retention indices are practical only for simple mixtures of pure compounds. For good qualitative analysis, gas chromatography should be combined with some other analytical system and often,

confirmation by two or more methods is desirable. Mass spectrometry is frequently a preferred choice because of its high sensitivity and relatively specific spectral information.[5]

Mass spectrometry is one of the finest tools available for the analysis of volatile mixtures. It is a rapid and precise method, uses sample sizes on the order of a few milligrams, and often facilitates identification of components, even if previously obtained mass spectra are not available for comparative purposes. Because mass spectra result from the fragmentation patterns of a molecule, the presence of various functional groups in the molecule usually produces predictably distinctive mass spectra.

The compatibility of the gas chromatograph and mass spectrometer lies in the fact that both instruments require a certain degree of volatility. The combination of the two is vastly more useful than either the gas chromatograph or mass spectrometer used singly. Mixtures with mass spectra which are overlapped can be easily separated on the gas chromatograph, and peaks which are only partially resolved by the gas chromatograph can still be identified by mass spectrometry.

The combination of a gas chromatograph with a mass spectrometer has proven to be extremely useful for the rapid and positive identification of unknowns in complex mixtures. The mass spectra of the components can be

scanned and recorded simultaneously with the running of the gas chromatograph. Since Gholke's[6] description of the technique, there have been several modifications and applications of the technique. These modifications have simplified the operation of the equipment and have made the spectral readings more precise and legible.

The combined gas chromatographic and mass spectrometric technique has also proven to be extremely useful in establishing methods for quantitative gas chromatography. Thus, it is an extremely useful tool for both qualitative and quantitative analysis purposes.

Spectra Physics SP 4000 Chromatographic Data System.[7]--The Spectra Physics SP 4000 is a multi-channel data system specifically designed to be used with gas and/or liquid chromatographs. An SP 4000 system consists of an SP 4000 Central Processor module, from one to sixteen SP 4020 Data Interface modules (one for each chromatograph) and from one to sixteen SP 4050 Printer/Plotters (at least one for every four Data Interfaces).

An SP 4000 Central Processor contains the computing program to perform all of the calculations for the entire system. In addition, memory for the storage or parameter files, sample data and post-run calculations procedures are in the Central Processor. A full alphanumeric keyboard and cathode ray tube (CRT) facilitates the entry, review and

editing of all file and run data as well as operating status and system diagnostics. Files are displayed in page fashion for ease of review and editing.

The SP 4000 computer data system has the capabilities to perform functions ranging from simple integration to post-run calculations. The post-run calculations for determining component concentrations are selected by the method number (MN) parameter in the component files. There are variations within each method and the selection is based on its applicability to sample material and the accuracy desired.

The method used for the quantitative analysis of the pyrolytic oil distillates was the normalization method. This method uses response factors. Thus, the area of each component is corrected for its detector response relative to a reference component in the calibration run. Because it is a normalization method, the total percent concentration of all chromatographable components in the sample must be known for greatest accuracy. This method does not require precise sample preparation and sample injections, but the calibration mixture should contain all of the components typical of an analysis sample. This method was used rather than the internal standard method since there was no room in the chromatogram for an internal standard peak. The normalization method using response factors accounts for

all the components in the mixture. We could not account for all the components in the pyrolytic oil distillate. The peak enhancement method would have been the appropriate one to use, but due to the unavailability of this method in the SP 4000 computer data system at the time samples were run, it was not used.

The normalization method used calculated the response factors (KF_i) and then used these response factors to calculate the percent composition (% $Conc_i$) of each component in the mixture, as illustrated below:

$$KF_i = \frac{Conc_i}{Area_i} \times \frac{Area_{I_s}}{Conc_{I_s}}$$

Where KF_i is the correction factor for the component i.

$Conc_i$ is the amount of pure component i in the calibration sample.

$Area_i$ is the area of the component i peak in the calibration run.

$Area_{I_s}$ is the area of the component selected in the KF reference peak.

and $Conc_{I_s}$ is the amount of component selected as the KF reference peak.

To calculate the % concentration, the following formula was used:

$$\% \text{ Conc}_i = \frac{KF_i \text{ X Area}_i \quad (XF)}{\sum_{i=1}^{n} (KF_i \text{ X Area}_i)}$$

where % Conc_i is the percentage of component i present in the analysis sample.

KF_i is the calibration factor for component i calculated in the calibration run.

Area_i is the area of the component i calculated in the calibration run.

XF is the total percentage of the analysis sample represented by the components in the chromatogram if less than 100.

and $\sum_{i=1}^{n} (KF_i \text{ X Area}_i)$ is the summation of all detector response corrected areas in the chromatogram.

EXPERIMENTAL

Materials

Condenser oil (Project B-469) was provided by the Engineering Experimental Station of the Georgia Institute of Technology.

Authentic samples were purchased from Fisher Scientific and Aldrich Chemical companies.

Helium of high purity was used as a carrier gas.

Reagent grade acetone was used as the solvent to prepare the mixture (48-90) for quantitative analysis.

Procedure

Vacuum Distillation[8].--Pyrolytic oil (condenser oil Project B-469) was vacuum distilled at 56°/14.5-188°/19.0 mm. At the higher temperature, significant decomposition occurred. Pyrolytic oil (192 g) was distilled to yield 87.2 gm (45.4% recovery) of a viscous yellow oil. The sample was labeled 25-1.

Gas Chromatographic Analysis.--The search for a column was made on the 720 F&M gas chromatograph equipped with a thermal conductivity detector. Helium of high purity was used as the carrier gas. Representative columns of different polarity were studied extensively. The columns were Carbowax 20-M (very polar), polyphenyl ether (intermediate in polarity), and SE-30 (non-polar). All of these columns were ¼" x 6'

and packed with the respective liquid phase on chromosorb W 60/80 mesh. The gas chromatographic conditions for the analysis of the pyrolytic oil distillates using the respective columns are given in Table 1. The analysis was successfully performed using a ¼" x 6' column packed with 3% SE-30 on chromosorb W 60/80 mesh. The gas chromatographic conditions were: an injection temperature of 275°; an initial column temperature of 80° and after programming a final temperature of 260°. Figure 1 is the standard chromatogram of the pyrolytic oil distillates (25-1) using the Varian A 90-P3 gas chromatograph.

The gas chromatograph was also used for the identification of peaks by the addition of a suspected constituent. Most of these components had been previously identified by gas chromatographic-mass spectrometric analysis, as presented below (see "Results and Discussion"). The gas chromatographic conditions were the same as above and the Varian A 90-P3 gas chromatograph was used throughout the study.

The pyrolytic oil distillate (25-1) sample was mixed with an authentic pure compound that was suspected of corresponding to a certain peak and a chromatogram was run. The height of the peak increased if the supposition was correct, while a new peak was found if the two compounds were not identical. Figure 2 is the chromatogram of 25-1 plus Veratroldehyde. The height of peak 20 in Figure 1 is

Table 1. Gas Chromatographic Analysis Conditions for the Pyrolytic Oil Distillates.

Gas Component	Column	Column Temperature	Detector	Number of Peaks
Helium	SE-30 60/80 mesh 6' x ¼"	80°, then programmed to 250° @ 8°/min	Thermal conductivity	20
Helium	Polyphenyl Ether 60/80 mesh 6' x ¼"	100°, then programmed at 8°/min to 250°	Thermal conductivity	5
Helium	Carbowax 20M 60/80 mesh 6' x ¼"	136°, then programmed at 10°/min to 250°	Thermal conductivity	3

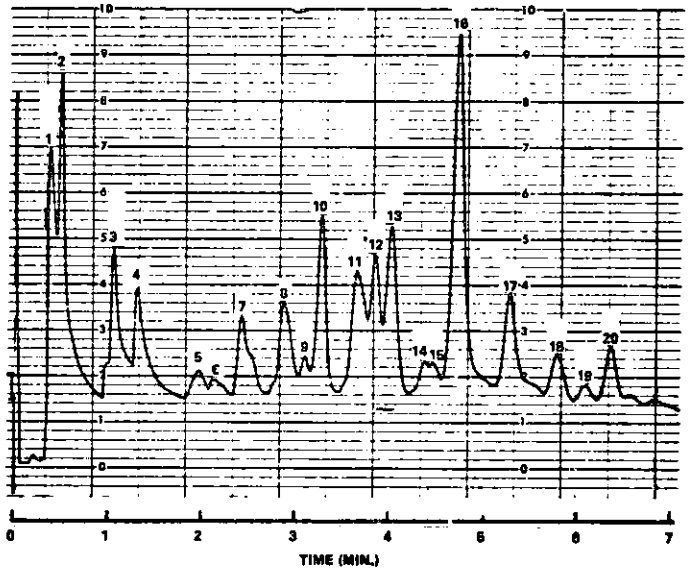

Fig. 1. Standard chromatogram of 25-1.

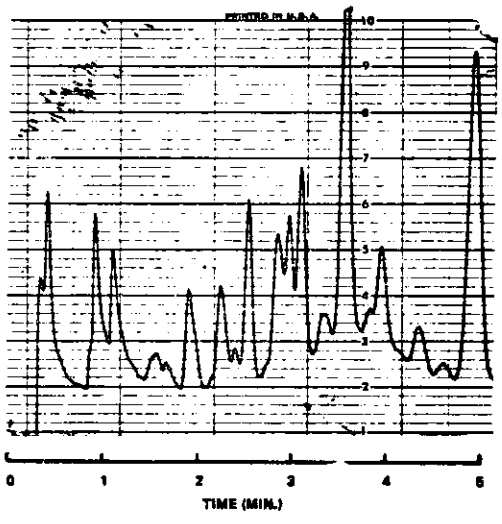

Fig. 2. Chromatogram of 25-1 plus Veratraldehyde.

increased in Figure 2 indicating the possible presence of Veratraldehyde in the mixture. This was done for several other compounds which were suspected to be in the mixture. The identity of each peak identified by using this technique is presented in the next section (see "Results and Discussion").

Gas Chromatographic-Mass Spectrometric Analysis.[9]--A Dupont Model 21-490 Gas Chromatograph-Mass Spectrometer (GC-MS) was used in this study. The chromatograph was equipped with a flame ionization detector and a column packed with 3% SE-30 on chromosorb W 60/80 mesh. Helium was used as the carrier gas. The gas chromatographic conditions for the analysis were: an injection temperature of 275°; an initial column temperature of 75° followed by programming at 10°/min to 300°; and a detector temperature of 300°. Figure 3 presents the GC-MS chromatogram of condenser oil.

By using this technique, a quantitative gas chromatographic method for the pyrolytic oils was developed.

A mixture of 25 components identified as present in the pyrolytic oil distillates was prepared by weighing μgm amounts of each. The mixture was labeled 48-90. Table 2 presents the list of components in 48-90. The sample was run on the GC-MS. From the GC-MS data, the identity of each peak and its relative retention time were established. This information (weights, relative retention times, and identity) for each peak was stored in the Spectra Physics

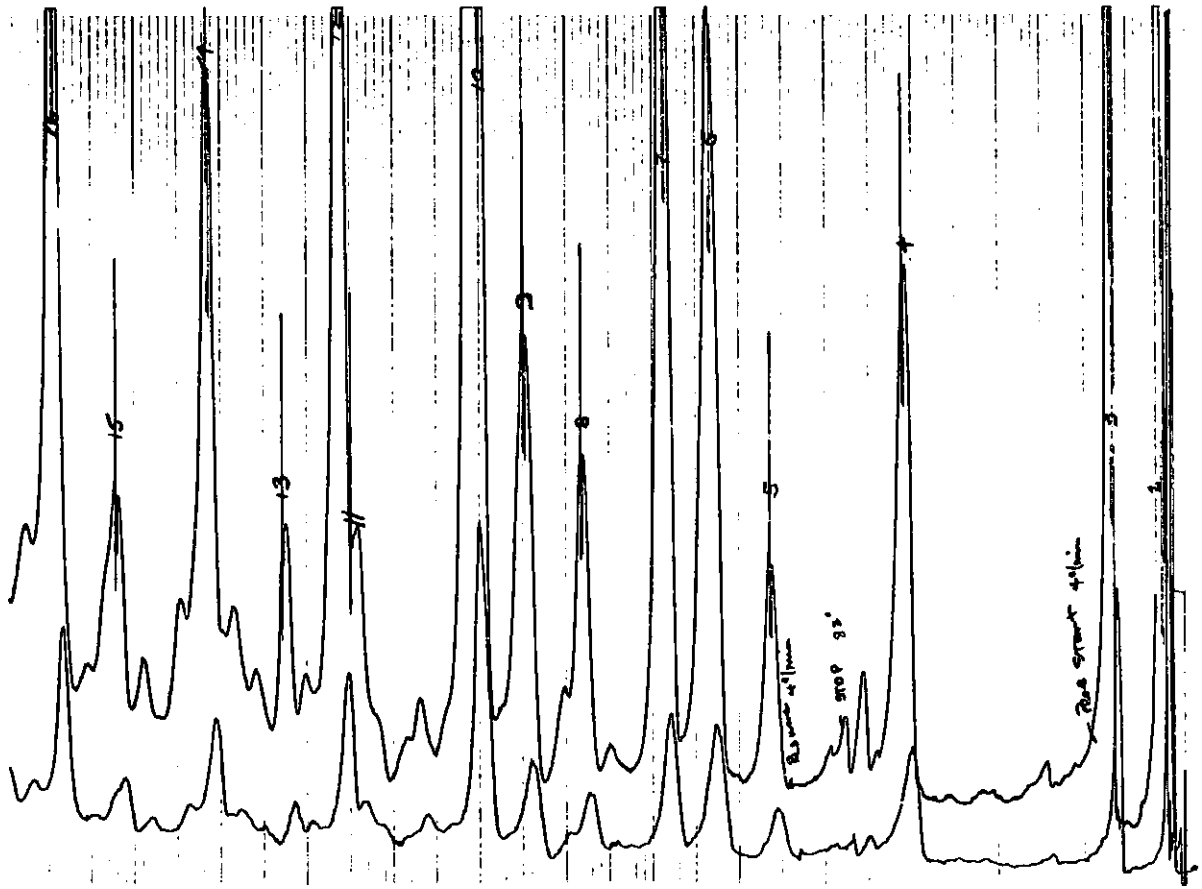

Fig. 3. GC-MS Chromatogram of Condenser Oil.

Table 2. List of Components in 48-90.

Compound	Amount Added (10^{-2}gm)
1. 1-Butanol	5.20
2. Veratrole	4.20
3. m-Cresol	6.13
4. Isoeugenol	9.23
5. o-Cresol	8.09
6. Guaiacol	12.09
7. m-Dimethoxybenzene	6.23
8. 2,5-Dimethoxybenzaldehyde	7.68
9. p-Dimethoxybenzene	14.07
10. p-Cresol	8.00
11. 1-Heptanol	6.14
12. Phenol	10.16
13. 4-Heptanol	5.30
14. m-Methoxyphenol	10.28
15. 2-Hydroxyacetophenone	4.09
16. 2-Hydroxy-4-methoxyacetophenone	16.12
17. p-Methoxyphenol	24.86
18. 2-Hydroxy-6-methoxybenzaldehyde, Furfural	16.44
19. 2,5-Dimethylfuran	5.96
20. Acetic acid	8.40
21. Isobutyl alcohol	7.46
22. Acetone	26.89
23. Propanol	6.14
24. Ethanol	9.06
25. 2-Hydroxy-4-methoxybenzaldehyde	8.71

SP-4000 computer data system and relative response factors were calculated relative to Guaiacol, which was used as the standard. All this data was stored in the SP-4000 computer data system and when the pyrolytic oil distillate was chromatographed, each peak was identified by means of relative retention time. By using the normalization factors, the relative amounts of each component identified to be in the pyrolytic oil distillates was calculated.

RESULTS AND DISCUSSION

Gas Chromatographic Analysis

The major effort at the beginning of this study was to develop gas chromatographic analysis conditions for the pyrolytic oil distillates. This was successfully accomplished using an F&M Model 720 Gas Chromatograph equipped with a thermal conductivity detector and a ¼" x 6' column packed with 3% SE-30 on chromosorb W (60/80 mesh). Helium was used as the carrier gas.

The gas chromatograph was also used for identification purposes. Identification of peaks was performed by adding a suspected constituent in the pyrolytic oil distillate and chromatographing the resulting mixture. Peak enhancement was observed if the pure component was present in the mixture. A number of peaks were identified using this technique and they are given in Table 3. (The numbers correspond to the peak numbers in Fig. 1, the standard chromatogram for 25-1.)

This method is not a satisfactory method for the identification of unknown components when used alone, but when used in conjunction with the mass spectral results which will be discussed below, it is a rapid means of identification of unknown components in complex mixtures.

Table 3. List of Compounds Identified by Enhancement Studies.

1.	Acetaldehyde
2.	Ethanol, acetone
3.	Isobutyl alcohol and acetic acid
4.	1-Butanol
7.	Furfural
8.	4-Heptanol
10.	1-Heptanol, phenol and 5-methylfurfural
11.	o-Cresol
12.	m-Cresol
13.	Guaiacol
16.	m-Methoxyphenol and/or p-methoxyphenol
18.	4-Hydroxy-3-methoxybenzaldehyde
19.	Isoeugenol
20.	4-Hydroxy-4-methoxybenzaldehyde

Interpretation of GC-MS Analysis Data and Assignment of Peaks

Using the GC-MS analysis data for 25-1, percentage tables (Table 4) were prepared for each mass spectrum. An analysis of these tables led to the assignment of peaks (Table 5). The numbers correspond to the peaks in Fig. 3 (the GC-MS chromatogram of 25-1).

The main techniques used in the interpretation of the percentage tables for assignment of peaks were the study of the fragmentation patterns and comparison with mass spectra of known compounds.

Examination of fragmentation patterns were often the only approach to the examination of mass spectra for compounds whose mass spectra were not available in the reference books.

Some difficulties were encountered in establishing the identities of compounds which had similar mass spectra or were incompletely resolved. This was specifically encountered in the identification of m-dimethoxybenzene, Veratrole, m-methoxyphenol and p-methoxyphenol, but their identities were established using gas chromatographic peak enhancement studies.

The compounds whose mass spectra were well documented in the reference books were identified by peak comparison. During the mass spectral comparison studies, there was some variation in relative peak intensities, but the mass spectra

Table 4. Percentage Tables for the Components in 25-1.[10]

Scan	m/e (Relative Intensity %)
1	29(11), 32(54), 39(2), 40(8), 41(4), 42(18), 43(41), 44(11), 45(12), 46(3), 47(2), 56(2), 60(3), 61(3), 71(3), 73(81), 74(100), 75(12), 117(2)
2	29(22), 31(10), 39(5), 41(27), 42(17), 43(61), 44(100), 45(24), 46(7), 73(31), 74(31)
3	29(25), 31(37), 32(72), 38(3), 39(6), 40(32), 41(17), 42(56), 43(100), 44(16), 45(20), 46(13), 48(7), 58(21), 59(9), 60(7), 72(12), 73(20), 74(8), 88(4)
4	29(9), 38(6), 39(11), 40(31), 41(19), 42(3), 43(3), 44(4), 45(5), 48(6), 51(7), 52(7), 54(5), 56(10), 62(3), 63(5), 64(9), 65(4), 66(26), 67(35), 68(4), 93(3), 94(100), 96(9)
5	29(26), 40(27), 41(51), 77(34), 79(36), 91(24), 107(72), 108(100), 109(9)
6	29(10), 38(4), 39(7), 40(22), 41(14), 42(9), 44(5), 45(5), 51(10), 52(16), 53(10), 54(14), 55(8), 56(8), 62(4), 63(8), 65(5), 69(5), 77(30), 78(10), 79(28), 80(12), 81(5), 90(5), 91(11), 92(17),107(85),108(100), 109(10), 131(4),132(4)
7	29(11),40(20),41(15),54(26),81(74),108(100),109(10), 131(4),132(4)
8	29(25),40(33),41(48),77(34),79(26),91(27),107(92), 121(50), 122(100)
9	29(19),40(26),41(31),52(22),77(33),78(12),79(13), 81(8),91(13),93(7),94(8),95(8),107(100),108(12),121(14), 122(56),123(17),126(9),127(13),128(76),129(12),138(12)
10	29(8),40(24),42(16),56(20),67(26),77(20),95(36), 123(84),138(100),139(10)
11	29(41),40(46),41(81),109(44),137(81),152(100),153(18)
12	29(6),32(93),40(12),41(9),65(9),77(11),91(13),94(10), 122(12),137(100),138(10),152(47),153(6)

Table 4. Continued

13	29(43),40(42),41(100),42(94),43(19),44(40),45(26), 52(18),54(27),56(38),58(21),65(20),67(32),69(55), 77(32),79(40),80(18),81(38),82(18),83(21),91(41), 92(19),93(48),94(19),95(26),105(29),106(20), 107(30),108(19),109(22),118(21),119(22),121(50), 122(19),134(36),135(19),136(19),138(22),148(19), 149(19),160(19)
14	29(15),40(24),41(21),77(30),91(19),133(24),134(22), 137(100),149(21),164(47),166(29)
15	29(49),40(48),41(87),56(55),77(57),91(49),149(72), 164(100),165(19)
16	29(9),40(14),41(11),56(28),65(13),77(32),91(27), 103(27),104(13),121(21),131(21),133(14),149(46), 164(100),165(13)

Table 5. Assignments of Peaks from Percentage Tables.

Scan	Components
1	Ethanol, Acetaldehyde, Isobutyl alcohol
2	Acetone, Acetic acid, Isobutyl alcohol
3	Phenol
5	o-Cresol
6	m- and p-Cresol
7	Guaiacol
8	2,4-Dimethylphenol
9	Veratrole, Naphthalene and Dimethylphenol
10	2-Methoxy-4-methylphenol
11,12	2,5-Dimethoxytoluene
13	Estragole and/or Anethole
14	2-Methoxy-4-propylphenol, Eugenol
15	Isoeugenol (cis)
16	Isoeugenol (trans)

of most compounds encountered had their own distinctive mass spectra, such that identification was very straightforward in most instances.

Quantitative Analysis

The GC-MS method was used to develop a quantitative gas chromatographic method for the pyrolytic oil distillates.

By using the GC-MS data of the standard mixture 48-90, the relative retention times and the identities of each peak were established. Table 6 gives the percentage tables and the assignments of peaks. Figure 4 is the standard chromatogram for 48-90, giving the relative retention times and the identities of each peak. Using this information, the response factors (Table 7) for all the components in the mixture were calculated. These response factors were relative to Guaiacol which was used as the standard.

By introducing all this information about the standard mixture 48-90 into the Spectra Physics computer data system, a quantitative analysis procedure for the pyrolytic oil distillates was developed. Figure 5 is the chromatogram from the quantitative run of the pyrolytic oil distillate 25-1 and Table 8 gives the concentrations of the components in the pyrolytic oil distillate.

Table 6. Percentage Tables and Assignments for the Components in 48-90.

Scan	Identity	m/e (Relative Intensity %)
1	Ethanol and acetone	26(16),27(50),29(44),31(100), 32(78),42(38),43(100),45(50), 46(20),57(100),58(34)
2	1-Propanol, acetone	25(60),26(100),27(100),29(100), 31(100),32(100),37(100),38(100), 39(100),41(100),42(100),43(100), 44(100),45(60),58(60),59(100), 60(100),61(100)
3	Isobutyl alcohol + 1-butanol	27(50),29(32),31(30),32(100), 39(22),40(16),41(50),43(100), 54(100),55(32),73(22),74(100)
5	Furfural	29(100),32(100),37(100),38(100), 39(100),40(80),42(50),74(40), 94(100),95(100),96(54)
6	Phenol	32(100),39(60),40(32),55(20), 65(54),66(78),94(100)
7	Phenol	29(40),32(100),37(38),39(100), 40(100),41(45),43(45),51(64), 52(45),56(10),63(78),65(100), 66(100),70(40),94(100),95(78), 96(8)
8	o-Cresol	32(100),39(34),40(16),51(25), 52(16),53(20),54(10),77(50), 79(54),80(25),107(100),108(100)
9	m-Cresol + p-Cresol	32(45),41(24),77(30),79(30), 107(90),108(100)
10	m-Cresol + p-Cresol	32(50),41(20),77(30),79(30), 107(80),108(100)
11	Guaiacol	32(90),39(50),51(34),52(34), 53(50),81(100),108(100),124(100)

Table 6. Continued

12	Guaiacol	32(100),39(30),77(22),78(20), 79(36),81(90),108(100),124(100)
13	m- and p-Dimethoxy-benzene	32(100),39(26),41(56),55(30), 64(30),65(30),66(26),96(100), 124(100),138(100)
14	Veratrole	32(80),39(30),41(40),51(12), 52(22),53(34),67(44),77(40), 96(64),107(26),108(50),124(58), 138(100)
15	m-Methoxyphenol	32(96),55(54),81(100),96(22), 97(22),108(100),124(100)
16	p-Methoxyphenol	32(80),39(40),54(58),81(100), 96(50),97(34),108(100),124(100)
17	2-Hydroxyaceto-phenone	27(34),29(30),32(80),39(34), 51(30),52(34),53(90),54(15), 55(14),64(26),66(26),81(78), 108(52),138(100)
18	2-Hydroxy-4-methoxy-benzaldehyde	32(80),39(34),54(34),56(15), 64(22),66(15),77(10),79(10), 80(10),81(15),96(30),108(52), 152(100)
19	Isoeugenol	39(24),51(24),53(24),55(29), 77(40),91(24),108(24),124(20), 141(18),151(29),164(100)
20	2-Hydroxy-4-methoxy-acetophenone	39(18),41(15),51(15),55(26), 77(30),91(40),105(22),122(16), 131(16),151(34),166(100)
21	2,5-Dimethoxy-benzaldehyde	39(26),41(15),43(58),51(24), 52(24),53(24),64(20),66(22), 71(22),77(15),79(20),80(15), 81(10),96(36),108(36),152(100), 164(100)
22	2,5-Dimethoxy-benzaldehyde	39(12),41(15),51(20),52(20),53(20), 54(26),66(18),77(18),79(12),80(12), 96(32),105(18),106(12),107(20), 108(12),121(20),124(24),152(100), 164(100)

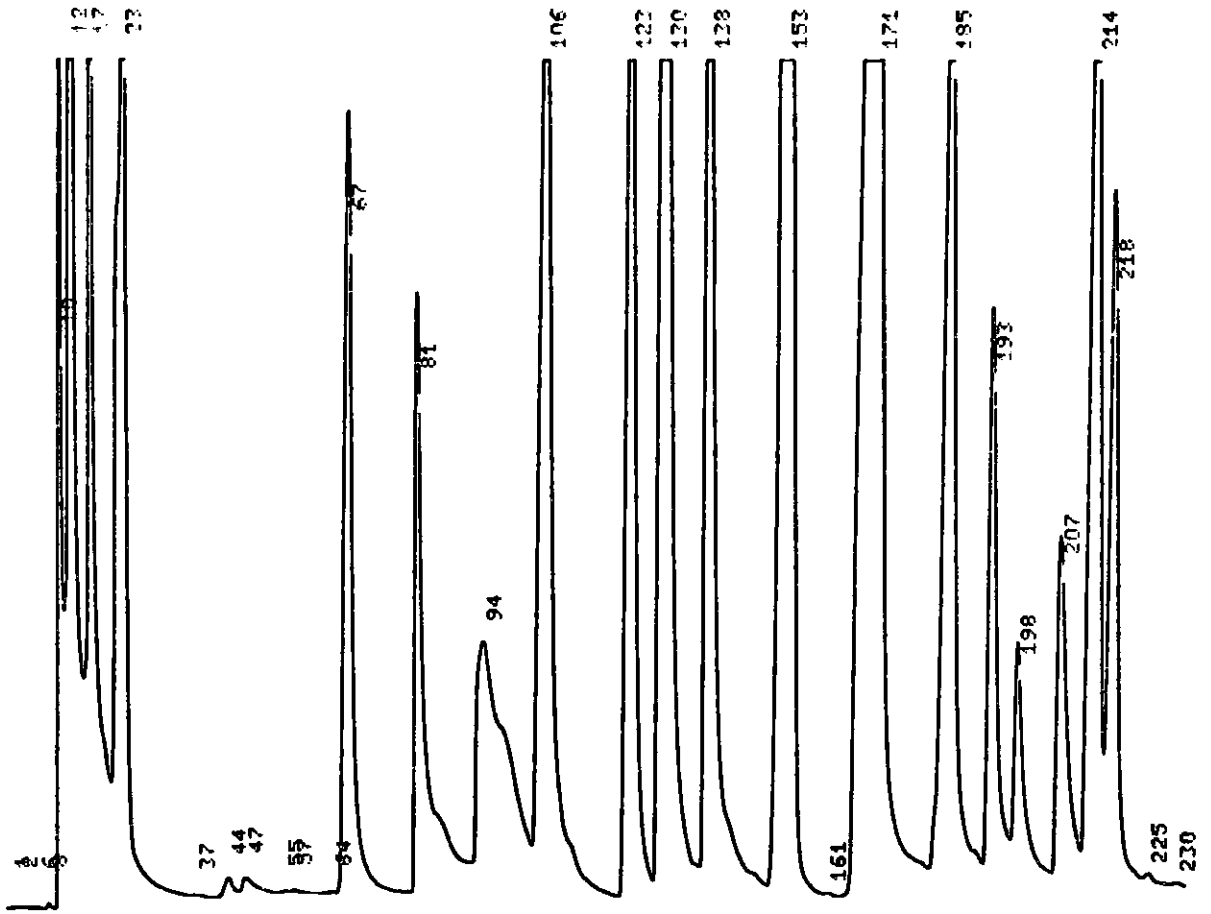

Fig. 4. Calibration Chromatogram of 48-90.

Table 7. Response Factors (KF) for the Components in 48-90.

Compound	Percent Concentration	Retention Time/Sec	Area	Response Factors	Relative Retention Time
Ethanol	5.426	10	51212	4.563	0.077
Isobutyl alcohol + 1-butanol	5.877	17	65515	3.864	0.474
4-Heptanol	2.49	67	90036	1.191	0.515
Furfural	3.829	81	73862	2.233	0.622
1-Heptanol		94	82484		0.723
o-Cresol	3.158	106	156595	.869	0.815
m-Cresol + p-Cresol	6.058	123	138709	1.881	0.946
Guaiacol	5.264	130	226770	1.000	1.000
m-Dimethoxybenzene + p-Dimethoxybenzene + Veratrole	10.4	153	280186	1.598	1.177
m-Methoxyphenol + p-Methoxyphenol	16.61	171	379471	1.886	1.315
2-Hydroxy-4-methoxybenzaldehyde	4.336	185	169613	1.101	1.423
2-Hydroxyacetophenone	3.032	193	90653	1.441	1.484
Isoeugenol	3.39	198	22611	6.459	1.523
2-Hydroxy-4-methoxyacetophenone	8.871	207	55715	6.858	1.646
2,5-Dimethoxybenzaldehyde	3.715	218	86379	1.000	1.677

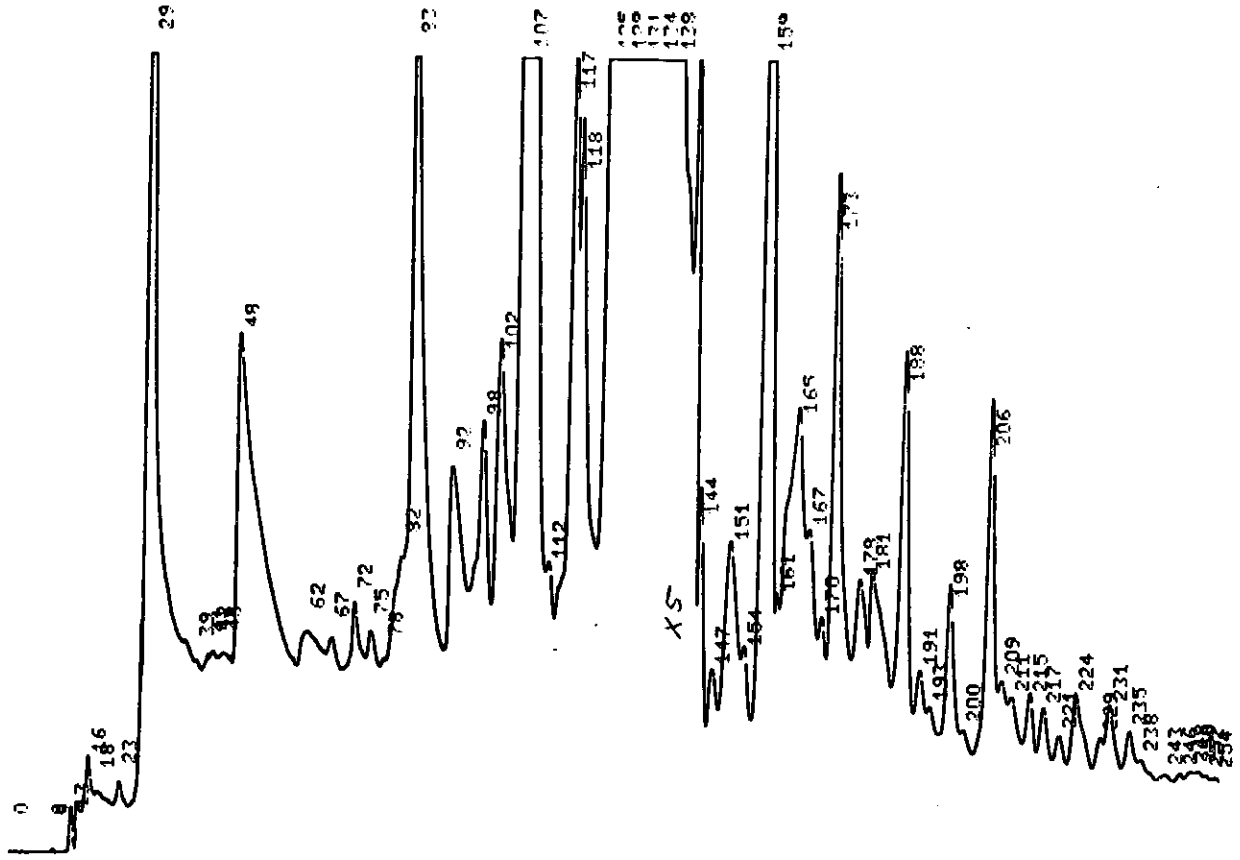

Fig. 5. Quantitative Run Chromatogram of 25-1.

Table 8. Quantitative Results for the Components in 25-1.

Compound	Percent Concentration	Retention Time/Sec	Area	Response Factors	Relative Retention Time
1-Propanol + Acetone	.061	16	1263	1.379	.116
Isobutyl alcohol + 1-Butanol	.164	18	1209	3.864	.13
2,5-Dimethylfuran + Acetone	3.113	29	30245	2.921	.21
4-Heptanol	.066	72	1581	1.191	.522
Furfural	2.263	83	28760	2.233	.601
1-Heptanol		98	8284		.71
Phenol	6.145	107	101924	1.712	.775
o-Cresol	.479	118	15640	.869	.855
m-Cresol + p-Cresol	7.561	131	114092	1.881	.919
Guaiacol	5.874	138	166756	1.000	1.000
m-Dimethoxybenzene + p-Dimethoxybenzene + Veratrole	10.34	159	183679	1.598	1.152
m-Methoxyphenol + p-Methoxyphenol	.74	178	11140	1.086	1.29
2-Hydroxy-5-methoxybenzaldehyde		191	24178		1.384
2-Hydroxy-4-methoxybenzaldehyde	.751	193	19369	1.101	1.398
2-Hydroxyacetophenone	.762	200	15008	1.441	1.449
Isoeugenol	5.206	211	22882	6.459	1.529
2-Hydroxy-4-methoxyacetophenone	4.925	217	20387	6.858	1.572
2,5-Dimethoxybenzaldehyde	1.23	224	33356	1.047	1.623

CONCLUSION

A GC-MS analytical procedure was developed for the volatile components of the pyrolytic oils obtained by the pyrolysis of pine bark and sawdust at the Tech Air Corporation in Cordele, Georgia.

The major components of the pyrolytic oil distillates are: acetaldehyde, ethanol, acetone, acetic acid, isobutyl alcohol, 1-butanol, furfural, 4-heptanol, 1-heptanol, phenol, o-cresol, m-cresol, p-cresol, Guaiacol, m-dimethoxybenzene, Veratrole, m-methoxyphenol, p-methoxyphenol, 4-hydroxy-3-methoxybenzaldehyde, Isoeugenol, 4-hydroxy-4-methoxyacetophenone and veratraldehyde.

A quantitative gas chromatographic procedure was also developed for the condenser oil distillates. The following results were obtained in the quantitative run of the condenser oil distillate: furfural (2.3%), phenol (6.1%), o-cresol (0.5%), m-cresol and p-cresol (7.6%), Guaiacol (5.9%), m-dimethoxybenzene, p-dimethoxybenzene and Veratrole (10.3%), m-methoxyphenol and p-methoxyphenol (0.7%), Isoeugenol (5.2%), 4-hydroxy-4-methoxyacetophenone and veratraldehyde (5%).

In general, the successful development and application of a GC-MS analytical procedure for pyrolytic oil distillates has demonstrated the usefulness of this method for routine laboratory work for the identification of unknowns in complex mixtures.

REFERENCES

1. Larry L. Anderson, "Energy Potential from Organic Wastes; A Review of the Quantities and Sources," Bureau of Mines Information Circular, 8549 (1972)

2. J. A. Knight, J. W. Tatom, M. D. Bowen, A. R. Coleord and L. W. Elston, "Pyrolytic Conversion of Agricultural Wastes to Fuels," 1974 Annual Meeting of the American Society of Agricultural Engineers.

3. J. A. Knight and M. D. Bowen, "Pyrolysis - A Method for Conversion of Forestry Wastes to Useful Fuels," Presented at Southeastern Technical Division of American Pulpwood Association.

4. L. F. Hawley and L. F. Wise, "The Chemistry of Wood," Chemical Catalog Co. (1926).

5. W. H. McFadden, "Combined Gas Chromatography and Mass Spectrometry - Application to Organic Analysis," John Wiley and Sons, Inc., N. Y. (1973).

6. R. S. Gholke, Anal. Chem., 31, 535 (1959).

7. Spectra Physics Chromatography Data System Instruction Manual (1977).

8. M. B. Polk, Atlanta University, Personal Communication, 1977.

9. T. W. Cole, Jr., Atlanta University, Personal Communication, 1977.

10. M. B. Polk, "Development of Methods for the Stabilization of Pyrolytic Oils," Annual Report, USEPA Grant, R8044-010, Atlanta University, Atlanta, Georgia, July, 1977.