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COMPARISON OF NON-VOLATILE BITUMINOUS RESIDUES AND COAL MATERIALS BY
PYROLYSIS GAS CHROMATOGRAPHY

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ABSTRACT

A study of non-volatile bituminous residues and coal materials by pyrolysis gas chromatography has been undertaken. The objective is to determine the coal and the coke precursors in a residue from the co-processing of coal and bitumen. This was investigated by quantifying eight model aromatic compounds and their co-eluting compound group in the pyrolysis products. Five samples consisting of Cold Lake coke, non volatile bituminous residue obtained from co-processing Forestburg coal with Cold Lake bitumen, Forestburg coal and a residual coal from liquefaction were pyrolysed from ambient temperature to 900°C, and the volatile products were analyzed by gas chromatography. Hydrocarbons up to C₇ have been detected in the gas region of the pyrogram, methane being predominant. The wide variety of polynuclear aromatic hydrocarbons produced by pyrolysis of these samples arise from the cleavage of their highly condensed aromatic structures. Naphthalene, phenanthrene and pyrene were abundant in the Cold Lake coke. On the other hand, indole and fluoranthene predominate in the Forestburg coal. Residual coal resembles Forestburg coal more than other non volatile residues.

LA PYROLYSE PAR CHROMATOGRAPHIE EN PHASE GAZEUSE, POUR ÉTABLIR
LA COMPARAISON ENTRE LES RÉSIDUS BITUMINEUX NON VOLATILS
ET LES MATIÈRES DE CHARBON

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RÉSUMÉ

On a entrepris une étude au moyen de la pyrolyse par chromatographie en phase gazeuse, pour comparer les résidus bitumineux non volatils et les matières de charbon. Elle vise à déterminer les précurseurs de coke et de charbon dans un résidu provenant du co-traitement du charbon et du bitume. On a mené cette ^{étude} ~~enquête~~ en quantifiant ^{dosant} ~~des~~ ^{huit} composés aromatiques ^{modèles} ~~en modèles~~ de ~~hauteur~~ et leur groupe de composé de co-élution dans les produits de la pyrolyse. Cinq échantillons, soit du coke de Cold Lake, un résidu bitumineux non volatil dérivé du co-traitement d'un charbon Forestburg avec un bitume de Cold Lake, du charbon de Forestburg et un charbon résiduel obtenu par liquéfaction ont été soumis à la pyrolyse, à partir de la température de la pièce jusqu'à 900°C; on a ensuite analysé les produits volatils par chromatographie en phase gazeuse. On a remarqué la présence d'hydrocarbures jusqu'à C₇, dans la région gazeuse du pyrogramme, le méthane ^{étant} ~~prédominant~~. La grande ~~vari-~~ ^é ~~été~~ d'hydrocarbures aromatiques polynucléaires produits par la pyrolyse de ces échantillons provient du clivage de leurs structures aromatiques hautement condensées. Le ^é ~~à~~ naphthalène, le phénanthrène et le ^é ~~à~~ pyrène se retrouvaient de façon plus abondante dans le coke de Cold Lake. D'autre part, l'indole et la fluoranthène prédominaient dans le charbon de Forestburg. Le charbon ~~rés-~~ ^é ~~iduel~~ ressemblait au charbon de Forestburg plus que d'autres résidus non volatils. On a obtenu des renseignements complémentaires sur la pyrolyse par chromatographie en phase gazeuse au moyen de la spectroscopie infra-rouge.

INTRODUCTION

Pyrolysis is one of the oldest methods of structural determination. Combined with gas chromatography, this technique provides immediate isolation of the pyrolysis products allowing them to be identified before they can be lost or altered in secondary reactions. Application of this technique to the study of coals, tars and petroleum pitches has generated considerable interest over the years (1-6). It has also been used to study the rank of coal from different sources (7).

Pyrolysis gas chromatography (PGC) of asphaltenes has been the subject of many publications (8-11). It has been reported (8-9) and also observed in our laboratory (12) that pyrolysis of asphaltenes at moderate temperature (350-400°C) leads to the cleavage of paraffinic side chains (up to C₃₄) linked to the aromatic cluster. At a higher pyrolysis temperature (450-900°C) the condensed aromatic ring system breaks into aromatic hydrocarbons.

In this study we applied PGC to the identification of the coal precursors in the residue from the co-processing of coal and bitumen. The five samples studied were Cold Lake coke, Forestburg sub-bituminous coal, a pitch (distillation residue boiling above 524°C) obtained from the co-processing of Cold Lake bitumen with Forestburg coal, tetrahydrofuran (THF) insolubles portion of the latter and residual sub-bituminous coal (THF insolubles) obtained from liquefaction of the coal with anthracene oil. Major peaks obtained from PGC were identified by comparison of the sample retention times with selected model polynuclear aromatic hydrocarbons (PNA) of different ring number. PGC was also used as a key technique to gain insight into coke, coal and co-processing pitch structures.

Infrared and elemental analyses of the samples supported the pyrolysis results.

EXPERIMENTAL

Samples

1. Cold Lake coke (completely insoluble in THF) obtained from hydroprocessing of Cold Lake bitumen at 450°C under 2000 psi (13790 kPa) pressure.
2. Forestburg sub-bituminous coal, Alberta Basin.

3. Pitch from the co-processing of Cold Lake bitumen and Forestburg coal
4. THF insolubles of sample 3.
5. Residual sub-bituminous coal (THF insolubles) obtained from co-processing Roseline Mine coal with anthracene oil at 450°C under 2000 psi (13790 kPa) pressure.

Apparatus

A Varian 6000 gas chromatograph equipped with a flame ionization detector was used in this work. The pyrolysis unit was a CDS 170 Pyroprobe with a platinum coil probe.

The column was a DB-5 coated fused silica column, 27 m x 0.02 mm. Helium carrier gas was maintained at 100 kPa. Data were recorded on a Spectra-Physics SP-4100 integrating unit.

Elemental analyses were obtained using a Perkin Elmer model 240 C.

Infrared spectra were recorded on a Perkin Elmer model 283 B spectrophotometer.

Procedure

Each sample was ground to < 20 mesh particle size. Approximately 2.5 mg of sample was packed between two pieces of quartz wool inside a 26 mm x 2 mm I.D. quartz tube. The tube was placed in the coil of the Pyroprobe and inserted into the injection port interface on the gas chromatograph. The interface and injector were maintained at 250°C and the detector at 350°C. The sample was pyrolyzed from ambient temperature to 900°C with a temperature rise of 1°C/m sec and held at the final temperature for 20 sec. The column temperature program was 5 min at 50°C, a temperature ramp of 5°C/min from 50°C to 325°C with a hold time of 10 min at the final temperature. The pyrolysis products were chromatographed using an air flow rate of 120 mL/min and hydrogen flow rate of 20 mL/min.

A standard solution of model polynuclear aromatic hydrocarbons in toluene was injected onto the column as a reference and for peak grouping under the same pyrolysis conditions.

RESULTS AND DISCUSSION

Physical constants and retention data on the PNA used for peak grouping are given in Table 1. The retention time data is the average of 10 runs. Maximum retention time deviation was 0.01 min for pyrene.

In the analysis of Athabasca bitumen by PGC, Ritchie et al. (2) describes each pyrogram as having three prominent regions: the gas region, the fingerprint region and the envelope region (Figs. 1-5). By carefully controlling the pyrolysis conditions (i.e., 900°C at 1°C/m sec, hold for 20 sec), these regions give an indication of the type of material being analyzed.

Gas Region

Under the experimental chromatographic conditions, the gas region is characterized by the group of peaks eluting in the first five minutes. These peaks correspond to alkyl hydrocarbons up to C₇, non-condensable gases and light aromatics up to trimethylbenzene (R.T. = 5.67 min). This region was not integrated and therefore comments are based on visual examination of the pyrograms.

The first wide peak is mainly methane as indicated by analysing pyrolysis gases using a 5A molecular sieve column under the same pyrolysis conditions. The methane peak for the Forestburg coal, and THF insolubles pyrograms (Figs. 1 & 2) are approximately the same size. These two samples show very small quantities of light hydrocarbons in the gas region. However, the THF solubles portion of the co-processing pitch sample shows the formation of large quantities of light hydrocarbons that elute in this region (Fig. 3). This result is also supported by the higher H/C ratio of the parent pitch sample (1.00) compared to the THF insoluble fraction (0.70) (Table 2).

There is a considerable increase in the total amount of material eluting in the gas region of the co-processing pitch (sample 3) compared to coal and residual coal (samples 2 & 5) (Figs. 1, 3 and 4). This increase, particularly the methane peak is generated from the THF soluble portion of the co-processing pitch.

This result is in agreement with the results of high temperature pyrolysis obtained by Ritchie et al. (2).

The process leading to the formation of Cold Lake coke removes most of the paraffinic material such as long alkyl side chains that would crack producing light gases. As indicated in the Cold Lake coke pyrogram (Fig. 5) the only significant products in the gas regions are methane and propane. This argument is also supported by the low hydrogen-carbon ratio (Table 2) indicating greater aromaticity within the sample.

Fingerprint Region

A visual inspection of the pyrograms (Figs. 1-5) indicates significant similarities and differences in the products. In the fingerprint region is the region, from 5 min to 49 min, the complex pyrolysis mixture is separated according to boiling point and chemical structure. The fingerprint region of the pyrograms is shown in Fig. 6 and 7. Because of the complexity of the pyrograms, no single peak or group of peaks is sufficient to compare the results. However, as per Glajch et al. (3) eight identified compounds and their co-eluting compound groups have been used to compare the pyrolysis products.

The retention times of eight model compounds are given in Table 1. The areas of the peaks, corresponding to the eight model compounds were summed and the area of each peak was expressed as a percentage of the total. Similarly, the areas of the eight compound groups co-eluting with the model compounds (numbered in Figs. 6 and 7) were summed and each area was expressed as a percentage of the total. The results are listed in Tables 3 and 4.

As shown in Table 3, Cold Lake coke has a high proportion of condensed naphthalene, indole, phenanthrene and pyrene structures, whereas the residual coal contained only a small amount of pyrene and indole (Table 4). Thus the content of the group co-eluting with pyrene and the indole in the THF insolubles is the result of bitumen coking reactions in that particular run. The high content of the group co-eluting with fluorene in co-processing pitch and the THF insolubles (13.78 and 26.88, Table 4) is provided by the residual coal (51.91). Similarly, biphenyl and fluoranthene groups are formed predominantly from the coal precursors.

Envelope Region

The envelope region is the region from 49 min to 70 min. Ritchie et al. in his work on the pyrolysis of bitumens attributed this zone to distillation phenomenon rather than pyrolysis phenomenon (2). This zone decreases with increasing pyrolysis temperatures.

The results obtained in the present study indicate a similar phenomenon. The significant rapid reduction in chromatographic resolution in this area, indicates a group of compounds of similar chemical structure and boiling points that are difficult to separate. These compounds originate from two sources. Most are highly condensed residual structures from the pyrolysis

process that are swept onto the column. They also originate from the high molecular weight compound samples that do not undergo pyrolysis but are "distilled" onto the column.

The physical characteristics of the pyrolysis chamber should also be considered. The sample is placed in a quartz tube and heated with a coil surrounding the tube. There is a time-constant involved in the heat transfer through the tube into the center of the sample. As indicated by Glam et al. (1), pyrolysis at low heating rates may cause part of the sample to cross-link during the period of temperature rise to the final constant pyrolysis temperature. This cross-linking binds material that would otherwise be able to escape as volatiles, whereas, rapid heating can raise coal samples to high temperatures without significant decomposition and pyrolysing them at a constant temperature.

This cross-linked material resulting from isomerization, may also contribute to the overall eluants in the envelope region. As pointed out by Ritchie et al. (2) in reality "the residence time of organic material in a hot zone will play an important part in determining whether distillation, isomerization or cracking predominates". The envelope region is particularly important in the Cold Lake coke and THF insolubles samples which suggest that the latter might originate from the bitumen coking reaction. This result is also supported by the IR results as shown below.

Infrared Analysis

Reducing the particle size to less than the minimum wavelength of radiation to be transmitted is a basic requirement to obtain sharp peaks and low background absorption. Karr et al. (13) developed a method of micronizing a blend of sample and KBr. This procedure was used to obtain the infrared spectra of all the samples (Fig. 8). An infrared spectrum of the Cold Lake bitumen used in the co-processing runs was also obtained for comparison with the co-processing pitch sample (Fig. 9).

Preliminary infrared spectroscopic examination of the samples (Fig. 8) showed a strong phenolic absorption band at 3450 cm^{-1} for the Forestburg coal and residual coal. This band is in agreement with the high oxygen content of these coals (Table 2). The two strong C-H absorption bands at 2845 and 2920 cm^{-1} for the Cold Lake bitumen (Fig. 9), the co-processing pitch and the Forestburg coal samples are characteristic of the paraffinic side

chains. These bands are less pronounced for the coal samples and have disappeared in the coal residue sample except for the band at 1450 cm^{-1} which is attributed to more stable naphthenic structures.

The absence of these two C-H stretches for the THF insolubles and Cold Lake coke is expected as the pyrolysis of these samples showed few peaks in the gas region.

The absorption band in the region of 1600 cm^{-1} is caused by planar skeletal vibration (C=C) of the aromatic ring. This band is particularly intense in the coal samples and virtually non-existent in the Cold Lake bitumen (Fig. 9).

CONCLUSION

The use of PCG for the differentiation of complex samples such as coal, coke and co-processing pitch seems to be promising. In this study we have shown that the co-processing pitch is composed of different polynuclear aromatic hydrocarbons arising from the coal and the Cold Lake coke. Infrared and PCG results have shown that the THF insolubles of the co-processing pitch correspond more closely to the Cold Lake coke than to the residual coal.

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FIGURE CAPTIONS

- Figure 1 Pyrogram of the Forestburg coal
- Figure 2 Pyrogram of the co-processing pitch sample
- Figure 3 Pyrogram of the THF insolubles sample isolated from the co-processing pitch
- Figure 4 Pyrogram of the Cold Lake coke
- Figure 5 Pyrogram of the residual coal
- Figure 6 Fingerprint region of the Forestburg coal and co-processing pitch pyrograms
- Figure 7 Fingerprint region of the Cold Lake coke and THF insolubles pyrograms
- Figure 8 Infrared spectra of the samples used in this work
- Figure 9 Infrared spectra of the Cold Lake bitumen

Table 1 - Model hydrocarbons used for peak grouping
pyrolysis gas chromatography

Compounds	M.W.	B.P.°C	Retention Time
			Δ Rt (min)
Naphthalene	136	218	21.14
Indole	117	254	24.42
Biphenyl	154	255	27.15
Fluorene	166	298	32.57
Phenanthrene	178	336	37.42
Carbazole	167	355	38.58
Fluoranthrene	202	384	43.57
Pyrene	202	393	44.70

Table 2 - Elemental analysis of the samples

Sample	Carbon, wt %	Hydrogen, wt %	Nitrogen, wt %	Oxygen, wt %	H/C
1	66.48	2.36	1.42	3.35	0.42
2	59.23	4.10	1.29	20.23	0.83
3	80.54	6.74	1.28	0.30	1.00
4	28.60	1.68	0.85	7.70	0.70
5	61.90	2.93	1.56	11.50	0.57

Table 3 - Comparison of the areas of eight model compounds
identified in pyrograms
(values are per cents of total area of the peaks)

Compound	Cold Lake coke	Forestburg coal	Co-processing pitch	THF Insolubles	Residual Coal
Naphthalene	29.01	18.88	15.41	17.73	14.24
Indole	25.31	32.35	23.80	8.10	2.68
Biphenyl	4.78	5.31	19.87	7.51	10.74
Fluorene	7.95	15.67	17.74	33.38	37.75
Phenanthrene	12.19	7.32	10.12	6.30	4.30
Carbazole	5.01	5.58	-	5.47	16.72
Fluoranthene	-	9.10	5.50	5.93	5.87
Pyrene	15.75	5.79	7.56	15.58	7.70

Table 4 - Comparison of peak groups eluting with the eight identified compounds (values are per cent of the total area of the peak groups)

Peak Group No.	Compound Group	Cold Lake Coke	Forestburg Coal	Co-processing Pitch	THF Insolubles	Residual Coal
1	Naphthalene	34.60	19.80	9.82	13.90	11.81
2	Indole	18.55	36.22	39.28	14.67	1.65
3	Biphenyl	3.50	10.17	18.08	8.57	13.26
4	Fluorene	5.83	11.26	13.78	26.88	51.91
5	Phenanthrene	12.25	9.26	11.85	6.95	2.67
6	Carbazole	3.70	3.03	-	3.35	10.35
7	Fluoranthene	-	4.94	2.55	3.63	3.63
8	Pyrene	21.57	5.32	4.64	22.05	4.72

FORETBURG COAL

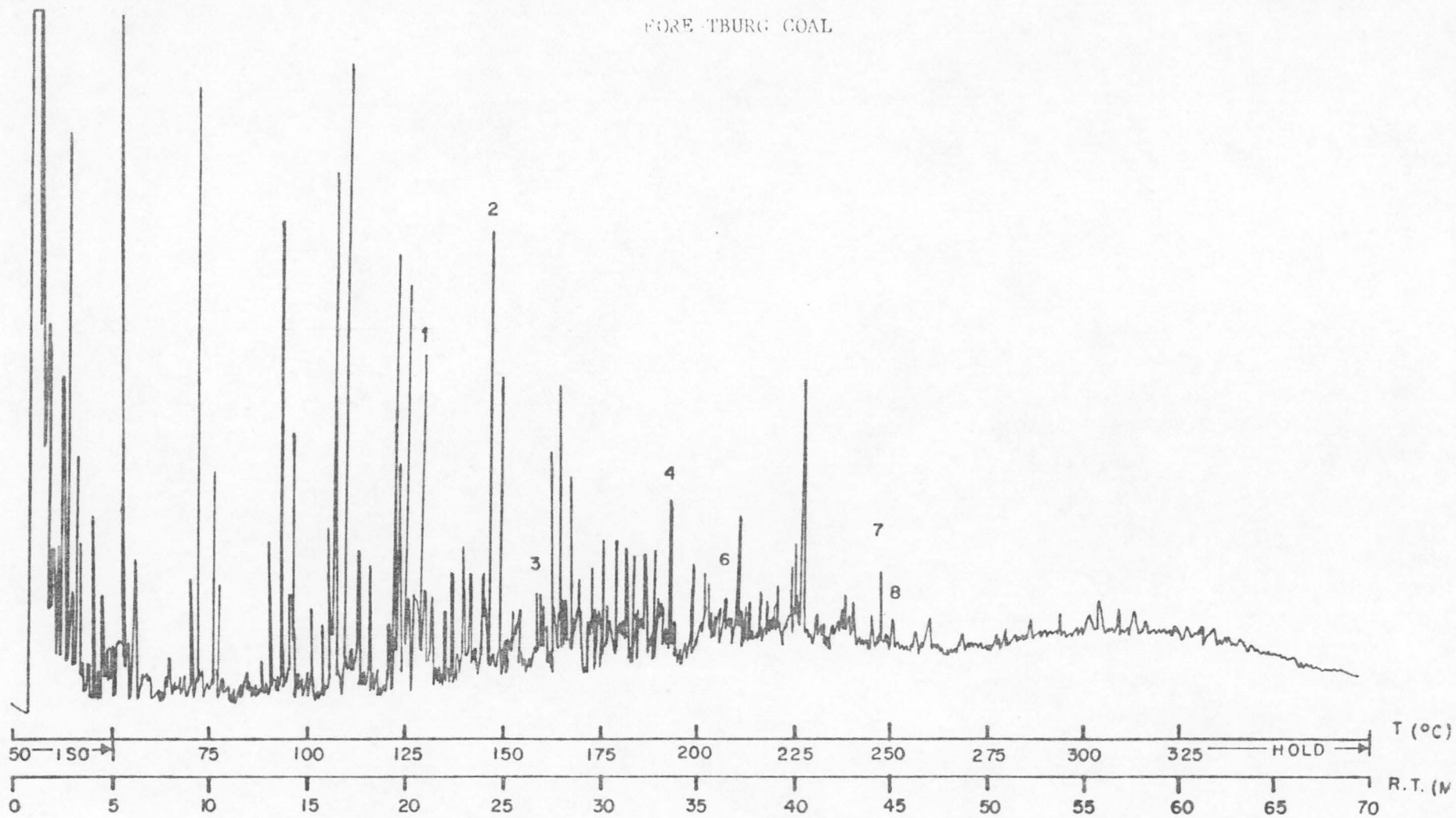


Fig. 1.

THE INSOLUBLES OF THE PITCH

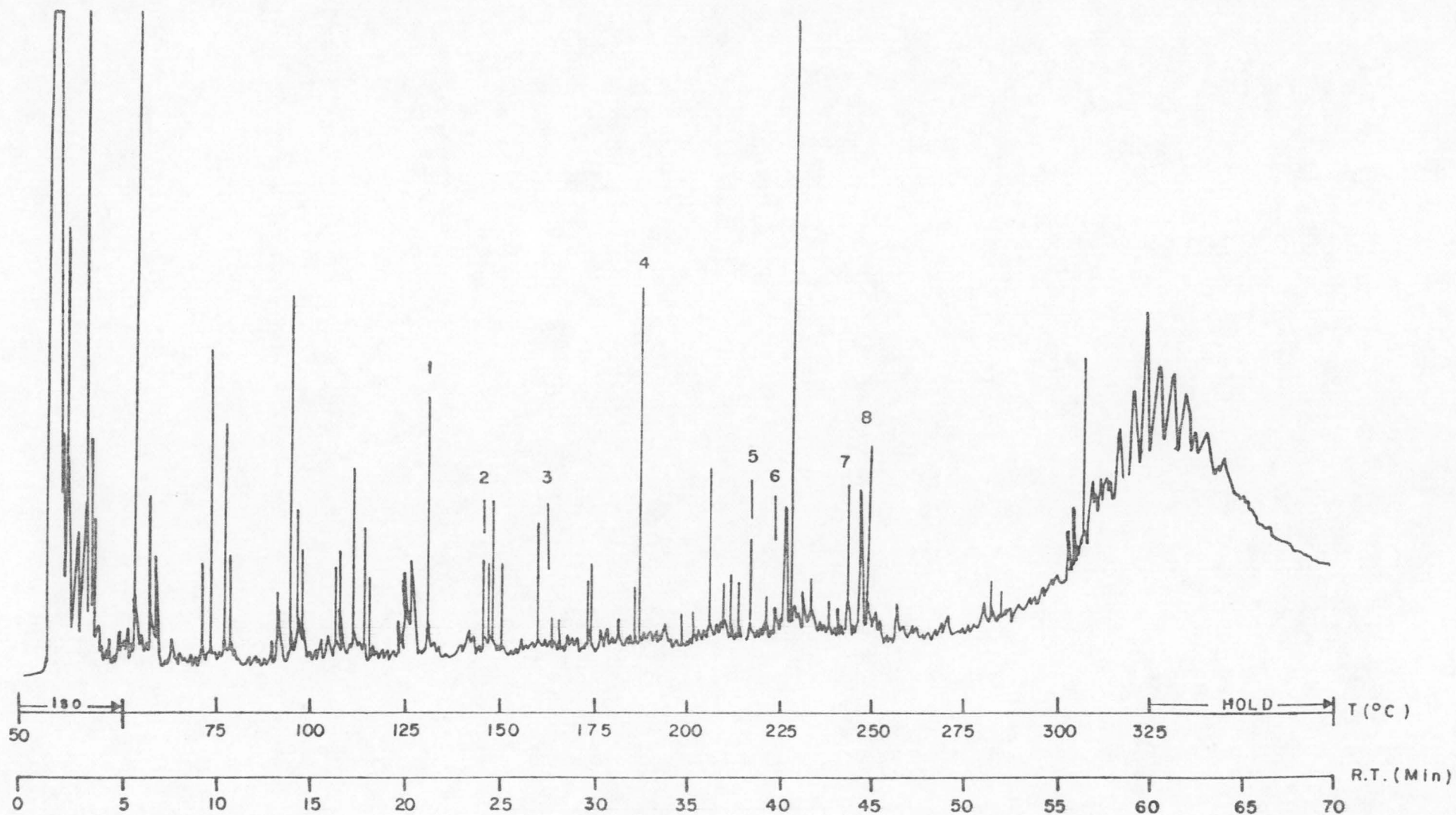


Fig. 2

CO-PROCESSED PITCH

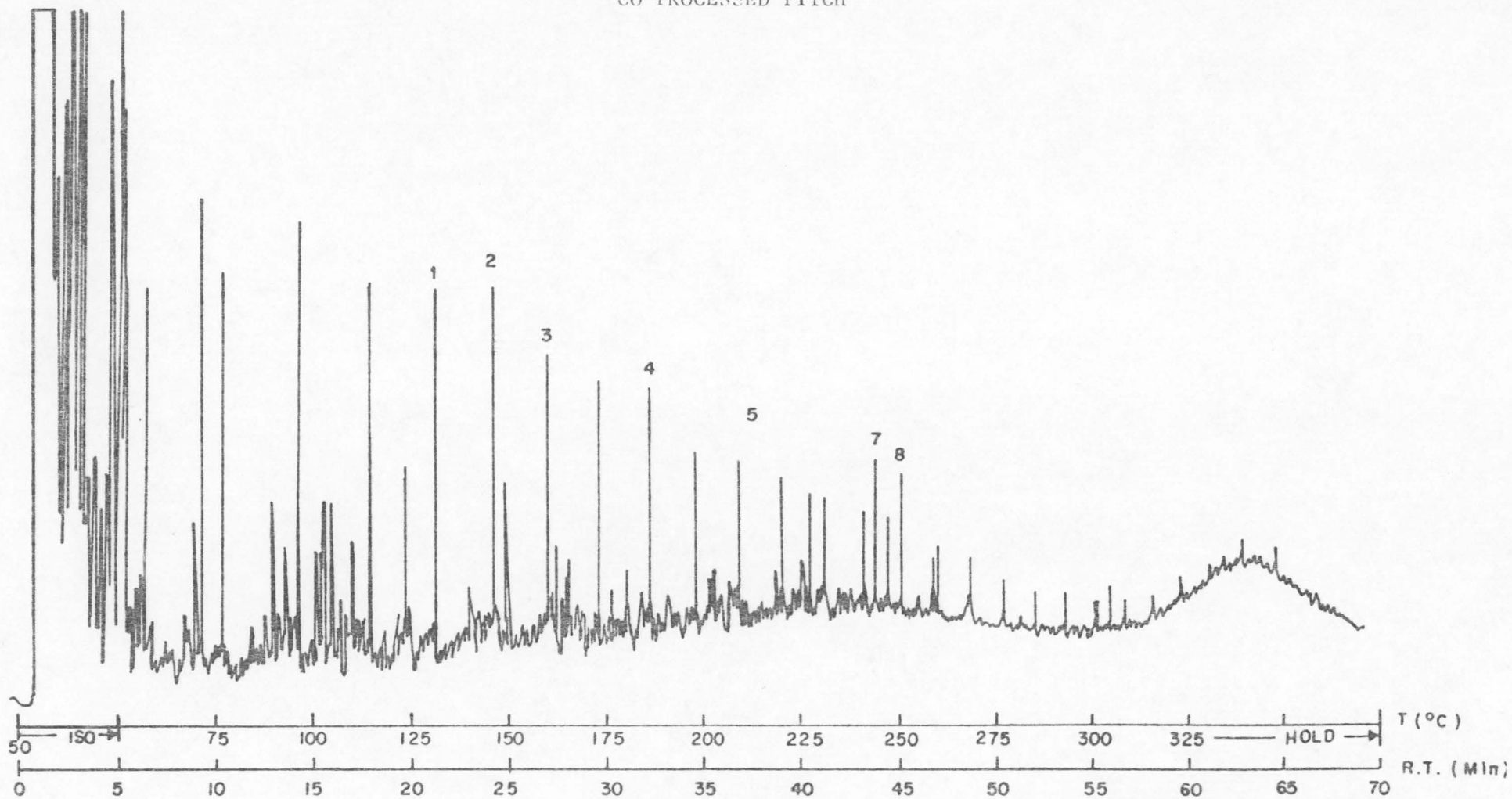


Fig. 3

RESIDUAL COAL (THE INSOLUBLE S)

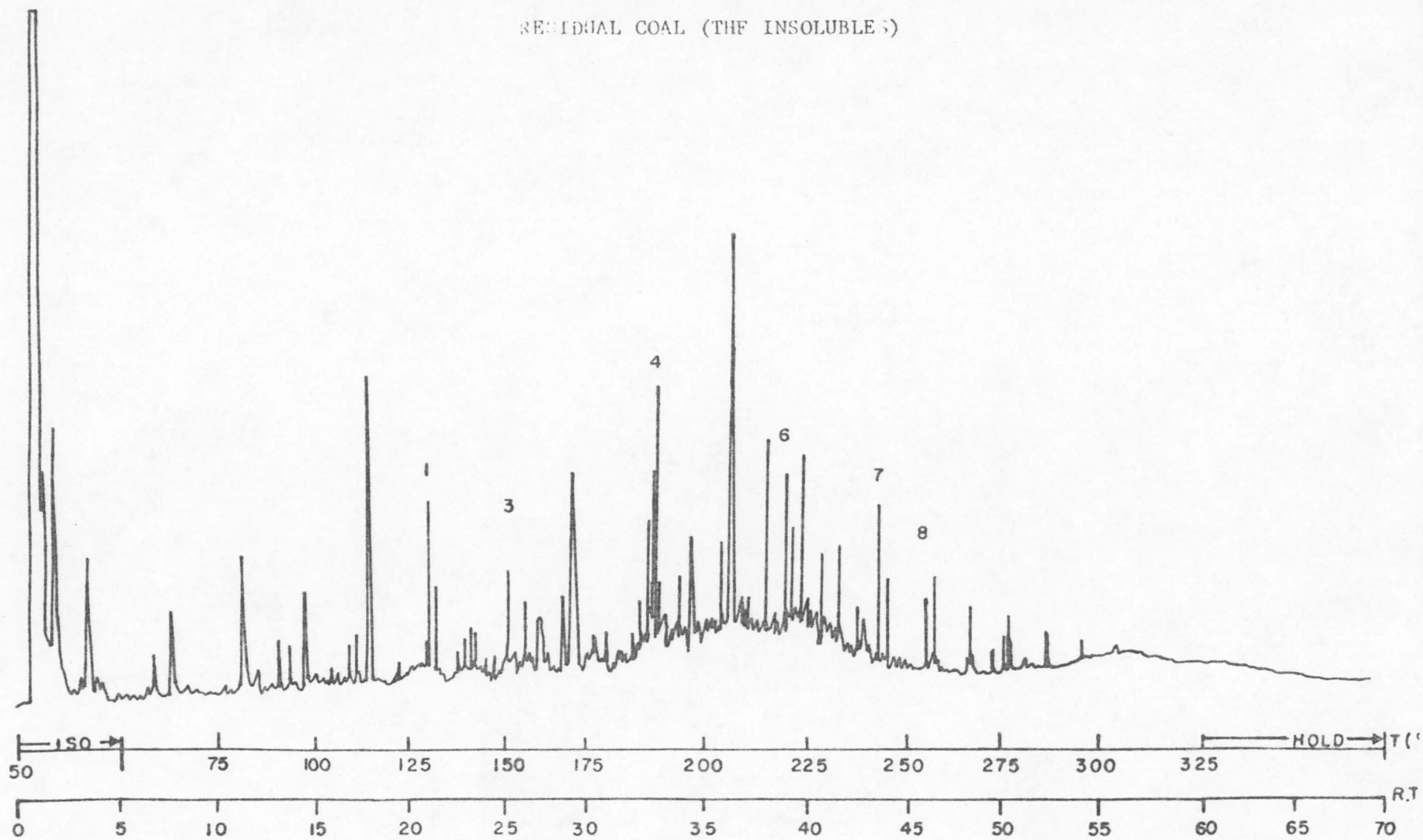


Fig. 4

COLD LAKE COKE

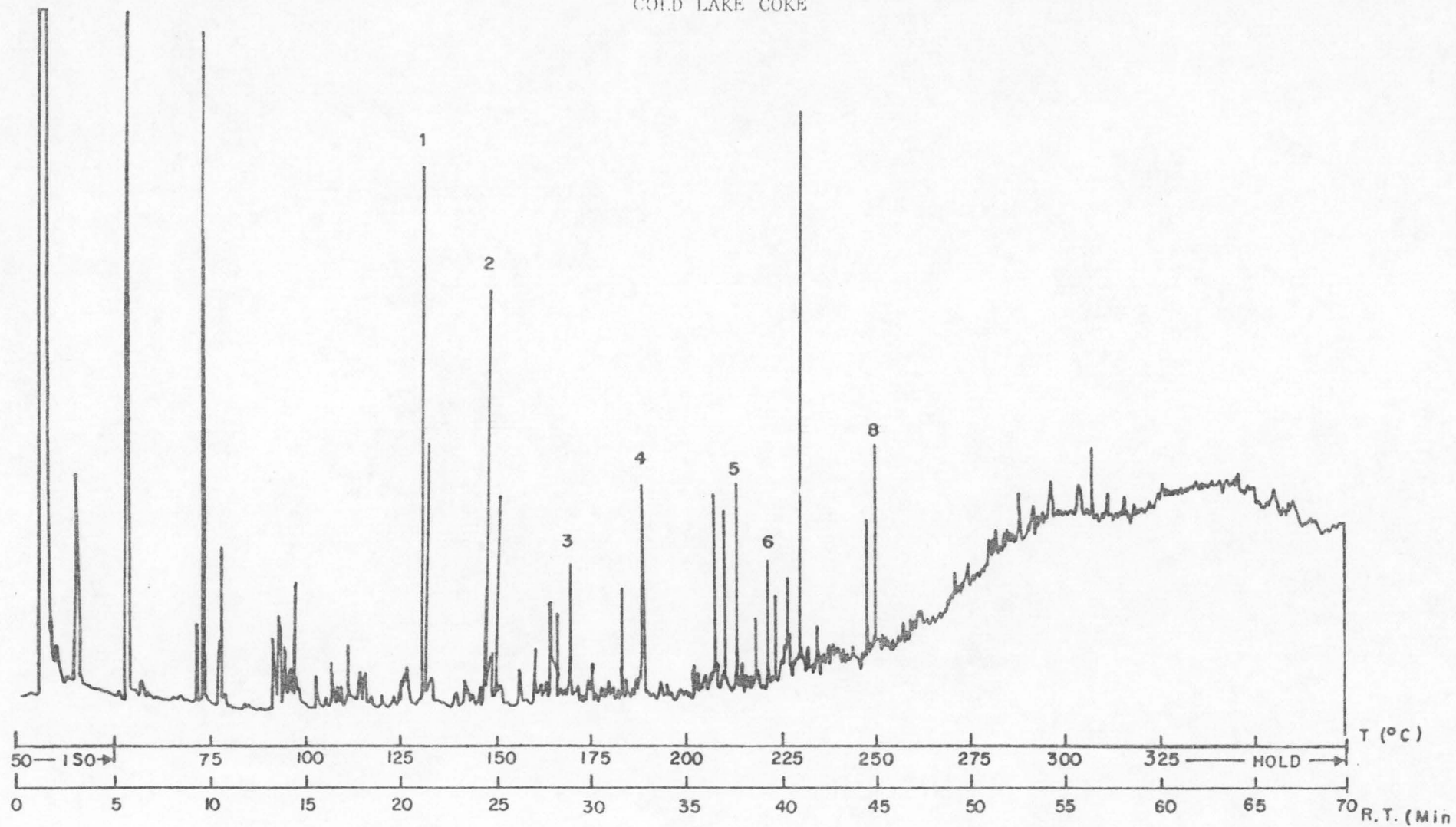
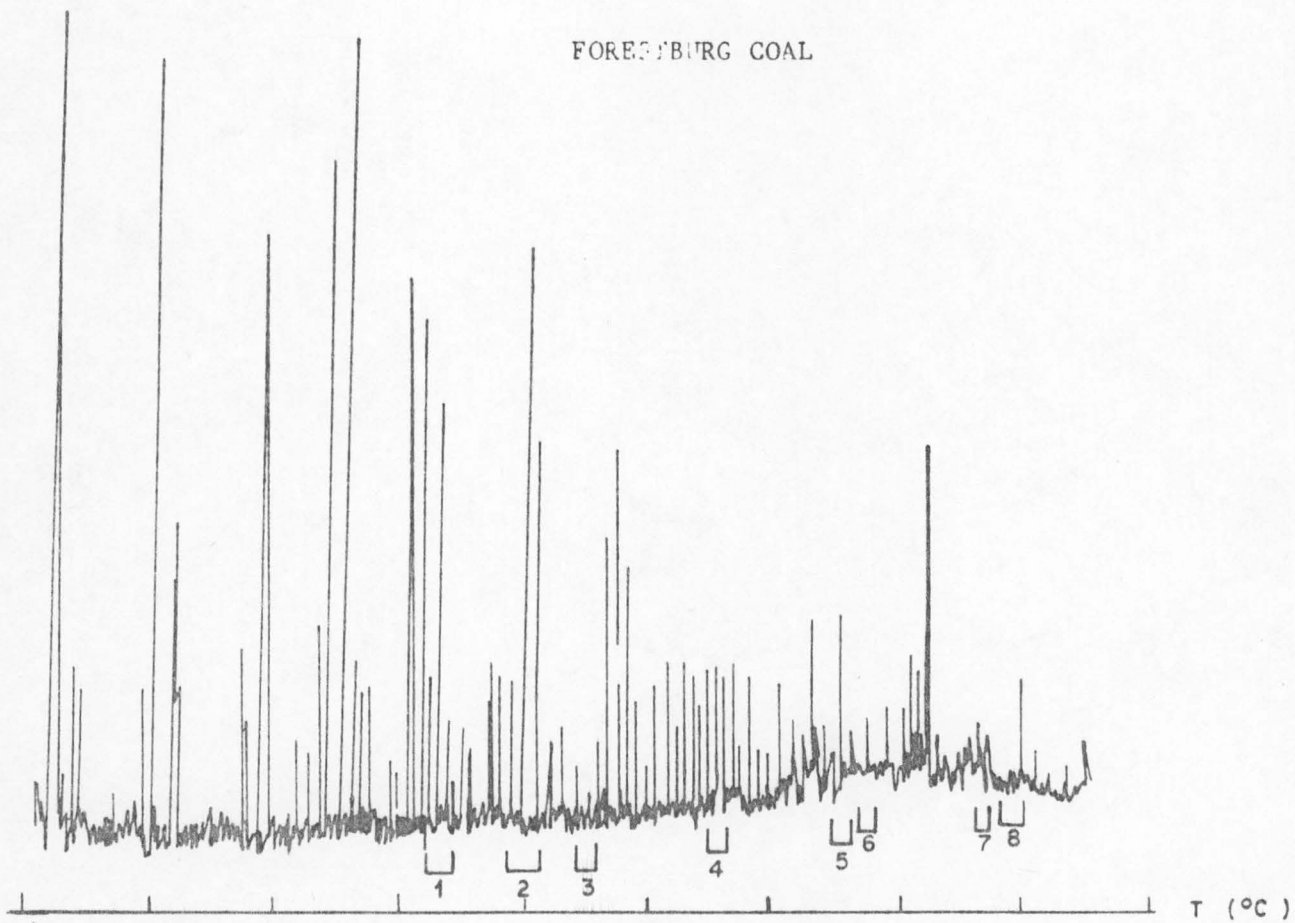


Fig. 5

FORESBURG COAL



CO-PROCESSED PITCH

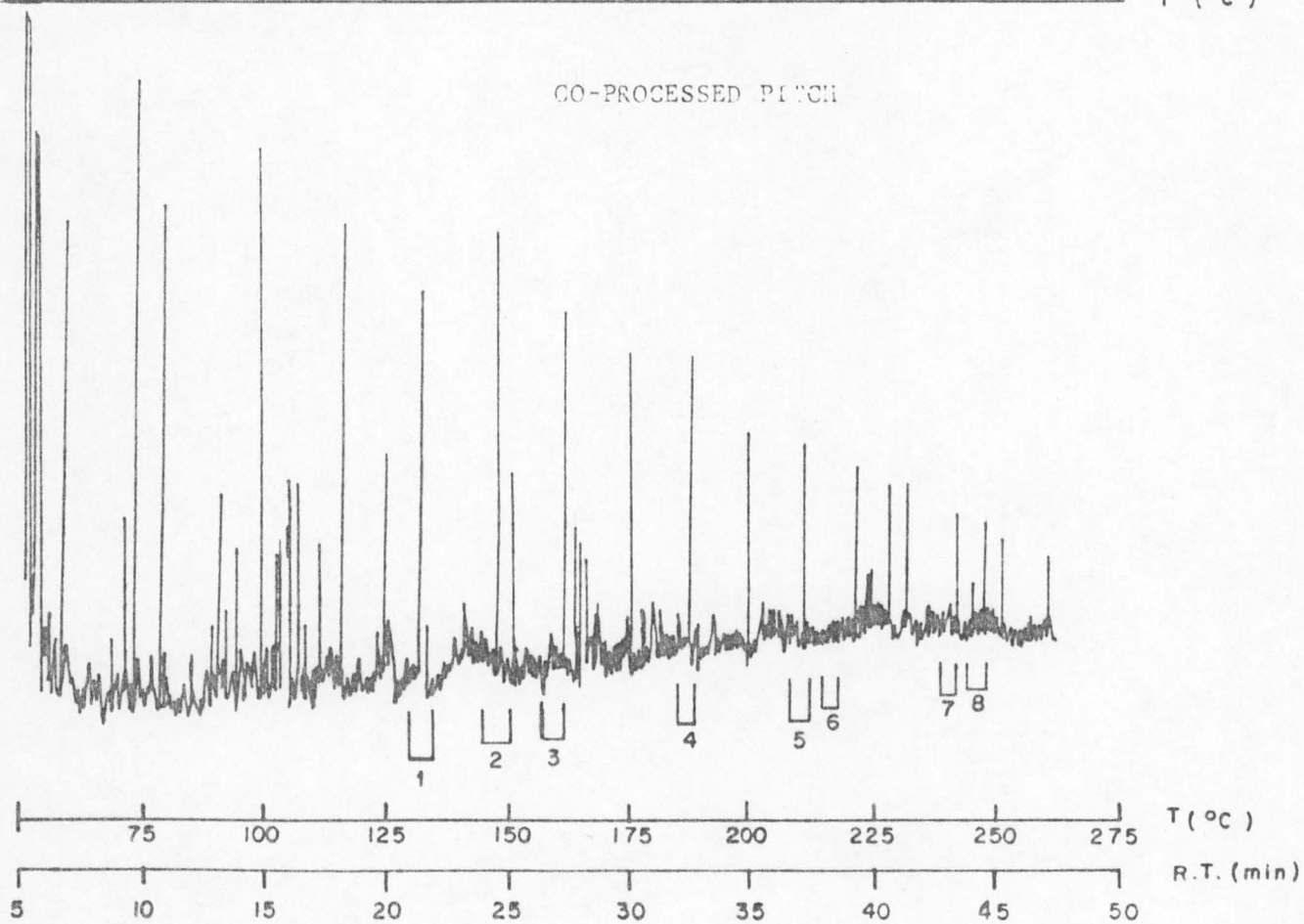


Fig. 6

(TOP) COLD LAKE COKE
(BOTTOM) THE INSOLUBLES OF THE PITCH

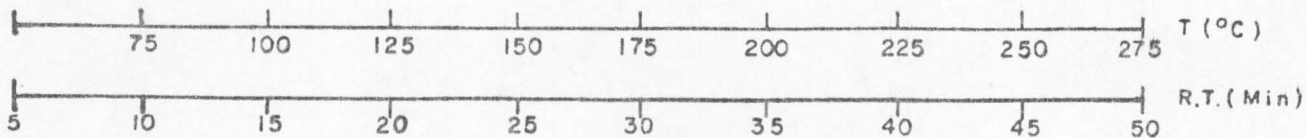
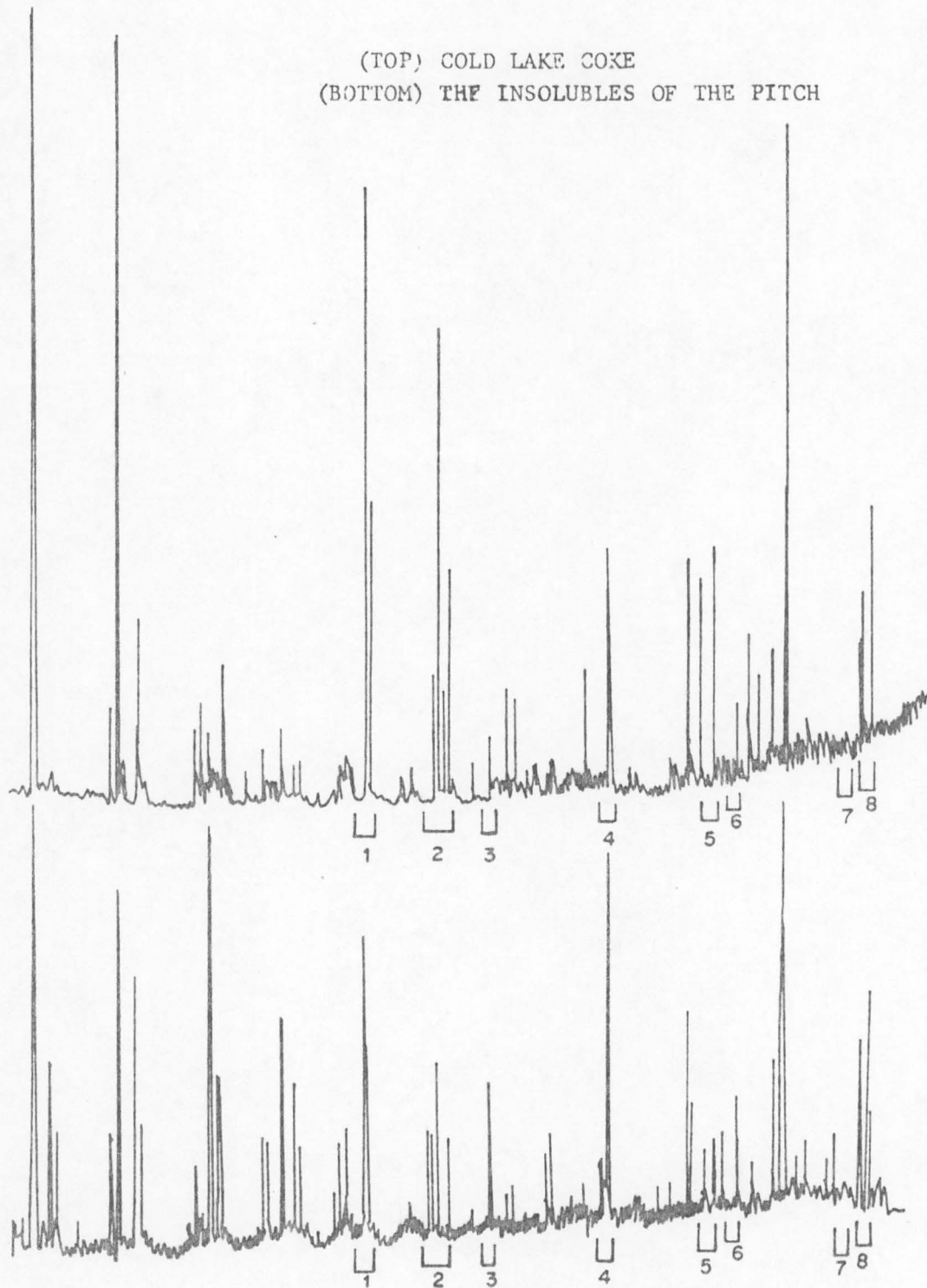


Fig. 7

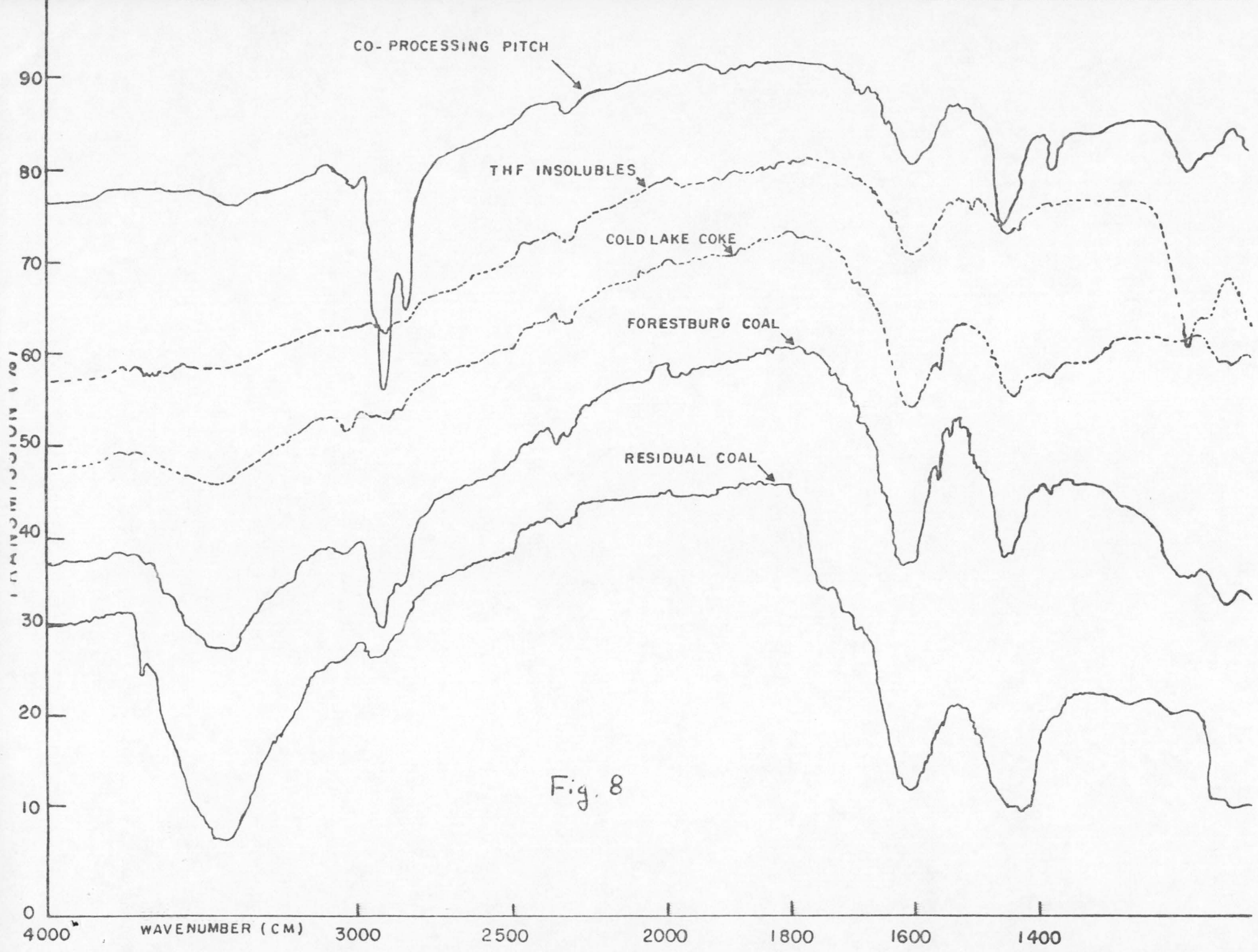


Fig. 8

