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PYROLYSIS GAS CHROMATOGRAPHY APPLIED TO COAL TAR- AND PETROLEUM-PITCHES

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SUMMARY

Pyrolysis gas chromatography has been used to study 12 coal tar- and petroleum-pitches used as binders and impregnants, respectively, in the production of thermic graphite electrodes. Parameters such as coking value, softening point and quinoline insolubles, which are normally used to characterize these pitches, have been related to changes in some of the peaks in the chromatograms. Computerized data collection and a nitrogen-specific detector, combined with a flame ionization detector, allowed for easy comparisons of different pitches and aided in the identifications of some of the pyrolysis products. The use of this technique for possible screening of unknown samples is suggested.

INTRODUCTION

The combination of pyrolysis and gas chromatography (PGC) was first demonstrated by Davison et al.[1] in 1954 for the study of polymers. In subsequent years, this technique has grown in importance for the fingerprinting and identification of polymers and paints, particularly in forensic applications[2-4]. Recently, PGC has been extended to microbiological samples and enzymes[5-8].

Coal tar-pitches are "obtained as a high aromatic, thermoplastic residue by the distillation of coal tar", and their properties and uses have been recently summarized by Collin and Kohler[9]. Petroleum-pitches are similarly obtained from the distillation of petroleum products, namely, decant oils and thermal tars. Both types of pitches find a wide variety of uses, including road building, production of technical carbon products, and, in combination with plastics, production of insulating and anti-corrosive materials[9]. One of the primary uses, however, is in the graphite industry as binders and impregnants in the production of thermic electrodes. King and Robertson[10] have compared coal tar-pitches with petroleum-pitches with respect to their

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usefulness as electrode binders. In addition, some of the pitches used in this study have been examined elsewhere using thermogravimetric analysis[11] and viscosity–temperature relationships[12].

Coal and petroleum samples have been studied using PGC by a number of authors, especially in the mid-1960s[13–18]. However, recent advances in pyrolysis units (allowing rise times of up to 20°/msec and final temperature of up to 1400°) and specific detectors for GC, in particular a nitrogen-specific detector, should allow substantial improvement of these earlier results. Computerized data acquisition was also available in the present work to provide easy comparisons of the complex chromatograms.

We have identified a number of the major peaks obtained from PGC and have correlated them to physically significant parameters. In particular, we have been able to relate our results to the coking value, softening point, and quinoline insolubles. The coking value is the most crucial since trends in the latter two parameters are often similar to those of the coking value. As a result, the use of this technique for the screening of pitch samples for the production of thermic graphite electrodes appears to be feasible.

EXPERIMENTAL

Materials

Ten coal tar-pitches and two petroleum-pitches were typical samples used in the graphite industry. The pitch numbering scheme corresponds to the one used elsewhere[11,12].

The column packing for the analysis was 3% OV-11 on 80–100 mesh Gas-Chrom Q (Applied Science Labs., State College, Pa., U.S.A.). A second column of 3% Dexsil 300 on 100–120 mesh Chromosorb W AW DMCS (Johns Manville, Denver, Colo., U.S.A.) was used for peak identification. Both columns were packed in stainless-steel tubing, 5 m × 2 mm I.D., which had been suitably washed in 50% nitric acid, water, chloroform, isopropanol and pentane.

Nitrogen was used as the carrier gas, and air and hydrogen as the detector gases. All three gases were purified by passage through silica gel and molecular sieve 5A (Linde).

Apparatus

The gas chromatograph was a Perkin-Elmer 3920 (Norwalk, Conn., U.S.A.) equipped with a flame ionization detector (FID) and a nitrogen–phosphorus detector (NPD). A Perkin-Elmer Dial-a-Flow controller was used to maintain the carrier gas flow. The pyrolysis unit was a Chemical Data Systems 190 Pyroprobe (Oxford, Pa., U.S.A.) equipped with a platinum coil probe.

Data collection and analysis were performed with a PDP 11/20 minicomputer (Digital Equipment, Maynard, Mass., U.S.A.) programmed in real-time BASIC using an Anscan analog-to-digital converter (Beckman Instruments, Fullerton, Calif., U.S.A.).

Procedures

Each pitch was ground to a 20-mesh (U.S. Series) particle size and pyrolyzed

in the solid form. A 2.4-mg sample was placed inside a 26 mm × 2 mm I.D. quartz tube with a glass wool plug in the back end of the tube to hold the solid. The tube was placed in the coils of the Pyroprobe which was then inserted into the injection port of the chromatograph. The sample was pyrolyzed from ambient temperature to 850° with a temperature rise of 20°/msec and held at the final temperature for 20 sec. The injector temperatures were 250 and 350°, respectively. Using the OV-11 column, the temperature program was: 4 min at 90°, a 4°/min ramp from 90 to 280° and a hold time of 32 min at the final temperature. The pyrolysis products were chromatographed using a carrier gas flow-rate of 35 ml/min. An air flow-rate of 90 ml/min was used with both detectors while the hydrogen flow-rates were 100 and 4 ml/min for the FID and NPD, respectively. The background bead current of the NPD was 20 pA.

Each pitch was run at least twice, with certain pitches run several times to determine reproducibility. Data were collected at one point/sec on both detectors, and the chromatograms were stored on DECTape for subsequent analysis.

A similar pyrolysis procedure was used with Dexsil 300 column for peak identification. Standard solutions of polynuclear aromatic hydrocarbons (PAH) in benzene were injected on both columns.

The pitches were characterized using the standard methods listed in Table I[19].

TABLE I

AMERICAN SOCIETY FOR TESTING OF MATERIALS STANDARD TESTS FOR PITCHES

Test	ASTM No.*
Softening point, SP (°C)	D-36
Sulfur (wt. %)	D-271
Benzene insolubles, BI (wt. %)	D-2317
Quinoline insolubles, QI (wt. %)	D-2318
Dimethylformamide insolubles, DMFI (wt. %)	D-2764
Coking value (wt. %)	D-2416

* See ref. 19.

RESULTS

Pitch characterization

The results of the standard methods of characterization for the 12 pitches are listed in Table II. The coking value is a measure of the usefulness of the pitch in the process of fabricating thermic electrodes. In general, the higher the coking value, the more useful the pitch in manufacturing the electrode. The softening point is an indicator of the ease of using the pitch in the process. However, because coking value increases as softening point increases, some balance between the desired carbon residue and thermal capability of the mixing equipment must be made before a given pitch is chosen for a particular graphite product. For obvious environmental reasons, a low sulfur content is desirable in any pitch.

The pitches used in the present study exhibited a wide range of values for the various standard tests, but they can be divided into three groups (labelled A, B, and C). This division follows the general pattern of high values for coking, softening

TABLE II

RESULTS OF ASTM TESTS FOR PITCHES

Group	Pitch	Coking value (wt. %)	Softening point (°C)	Sulfur (wt. %)	Benzene insolubles (wt. %)	Quinoline insolubles (wt. %)	Dimethylformamide insolubles (wt. %)
A	6	74.2	156.0	0.50	45.2	22.6	53.9
	6A	73.8	154.1	0.46	44.7	21.7	50.9
	5	69.5	136.2	0.50	41.7	21.7	46.9
	4	67.6	130.0	0.49	40.0	17.6	44.2
B	2	58.8	103.5	0.65	31.5	14.3	34.3
	2B	58.7	103.2	—	31.4	12.6	—
	2A	57.5	103.8	0.61	33.6	12.7	33.3
	1A	57.1	100.8	0.53	24.7	11.1	31.0
C	2C	53.4	105.1	0.34	34.0	5.4	34.7
	PP1	52.5	114.0	3.09	8.4	0.42	14.9
	ø	51.6	79.5	0.51	28.2	12.2	31.0
	PP2	50.7	104.2	4.2	23.8	4.3	30.7

point, quinoline insolubles (QI), benzene insolubles (BI), and dimethylformamide insolubles (DMFI) for group A; low values of these five parameters for group C; and intermediate values for group B. These groupings also correspond roughly to the use of the pitches in the process of electrode fabrication, with those in group A generally being the most desirable and those in group C the least desirable. Indeed, the pitches in group C are generally used as impregnants, while the other two groups are used as binders. A more detailed discussion of the importance of each of the parameters in electrode manufacturing is contained in two recent articles[11,12].

PGC

A typical chromatogram for PGC using both the FID and NPD results is shown in Fig. 1 for pitch 6A. The FID plot shows a number of major peaks, eight of which were used in the specific analyses to be discussed later. The NPD plot is less complex, but still exhibits a few peaks which occur in all of the samples. Since the FID was more reproducible than the NPD, the latter detector was used only qualitatively and as an indicator for peak identification, while most of the final correlations were done using the FID data. We were able to identify, using the OV-11 and Dexsil columns and the standard PAH solutions, three peaks in the NPD chromatograms and nine peaks in the FID chromatograms.

Although many of the same peaks occurred in all 12 pitches, an examination of three selected FID plots in Fig. 2 (one from each group A, B, and C) revealed that the general appearance of the chromatogram changed, particularly between pitches that were unlike using other standard characteristics (see Table II). The fact that these discrepancies were due to the differences in pitch composition can be seen by examining Fig. 3, where pitches 2B and 2 have very similar physical characteristics and almost identical chromatograms.

In our general approach to the analysis of these chromatograms, we found that no comparison based on a single peak or group of peaks was sufficient by itself
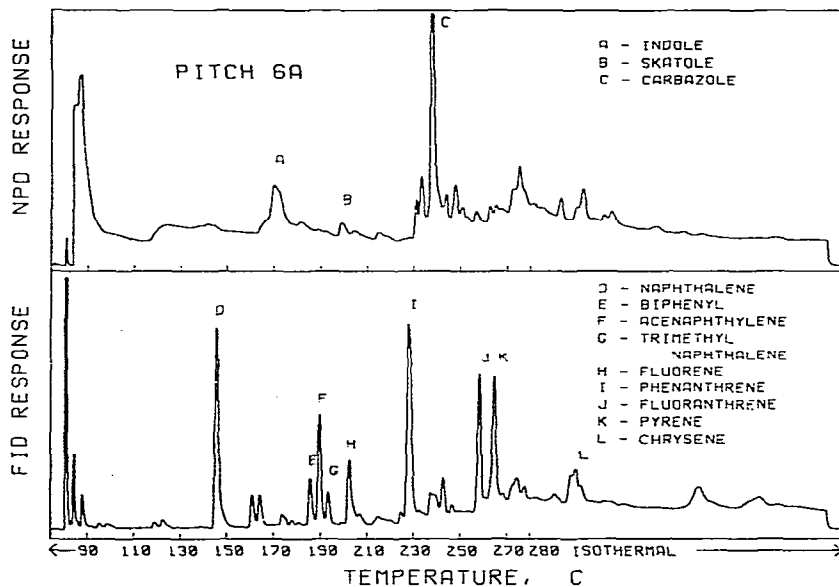
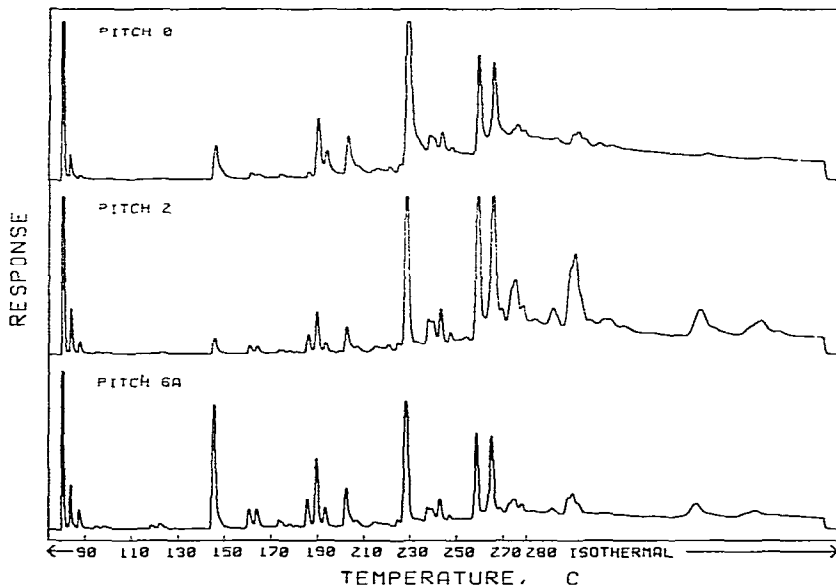Fig. 1. PGC chromatogram of coal tar-pitch 6A with major peak identification.

Fig. 2. Comparison of three coal tar-pitches. Pitch ⌀ from group C, pitch 2 from group B, and pitch 6A from group A. Flame ionization detector.

to distinguish and segregate them into groups similar to those in Table II. However, four independent comparisons could be used successfully.

Seven main peaks selected for study are labelled in Fig. 1 and were later identified as follows: D, naphthalene; E, biphenyl; F, acenaphthylene; H, fluorene;
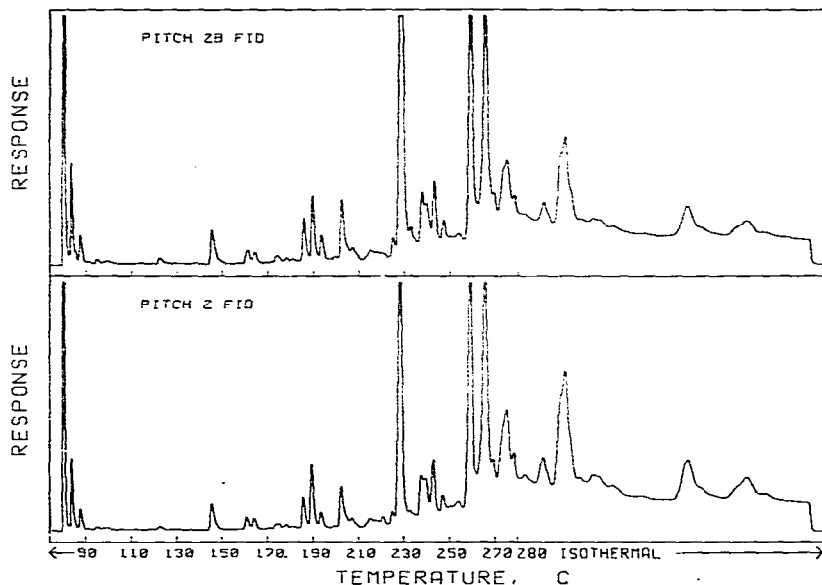
Fig. 3. Comparison of two similar coal tar-pitches, 2B and 2. Flame ionization detector.

I, phenanthrene; J, fluoranthene; and K, pyrene. The heights of these seven peaks were first summed and then the height of each peak was expressed as a percentage of the total. The results of this analysis are listed in Table III.

The most important observation is that for the more useful pitches, group A, all seven peaks were present in amounts of at least 4% and no single peak or group of peaks dominated the chromatogram. In contrast, for the group C pitches, the phenanthrene, fluoranthene and pyrene peaks dominated the chromatogram (see Fig. 2,

TABLE III

COMPARISON OF SEVEN MAIN PEAKS

Values are percent of the sum of the total peak heights of the seven peaks.

Group	Pitch	Coking value (wt. %)	Naph-thalene	Biphenyl	Acenaph-thylene	Fluorene	Phenan-threne	Fluo-ranthene	Pyrene
A	6	74.2	9	9	15	4	14	23	26
	6A	73.8	21	5	12	7	22	16	16
	5	69.5	8	8	12	4	17	25	26
	4	67.6	6	4	6	4	24	28	27
B	2	58.8	3	4	7	5	27	27	27
	2B	58.7	4	5	7	7	26	26	26
	2A	57.5	3	2	4	5	29	29	29
	1A	57.1	3	5	17	4	23	23	24
C	2C	53.4	1	—	—	2	31	33	33
	PP1	52.5	6	1	—	4	32	17	39
	ø	51.6	6	2	11	8	29	23	21
	PP2	50.7	3	—	—	—	10	25	62

pitch Ø, where the latter portion of the plot was substantially greater in area than the earlier portion). Indeed, for many of the group C pitches, some peaks were totally absent, acenaphthylene being a notable example. As expected, the group B pitches appeared to exhibit behavior between the other two groups.

Although these initial observations gave some correlation to the physical properties of the pitches, these results were not conclusive. For example, pitch Ø resembled the group A pitches in this initial comparison, and only secondary characterizations given below could differentiate it from the more useful pitches. Therefore, we decided to supplement this primary characterization with three secondary characteristics listed as I, II, and III in Table IV.

TABLE IV

SECONDARY CHARACTERIZATION

| Group | Pitch | Coking value (wt. %) | I | II | III | | |
			Phenanthrene/ naphthalene	Subareas 2/1	Biphenyl	Triplet acenaphthylene*	Trimethyl- naphthalene
A	6	74.2	1.7	1.48	34	59	7
	6A	73.8	1.0	1.27	25	57	18
	5	69.5	2.0	1.81	37	53	10
	4	67.6	3.9	2.66	36	50	14
B	2	58.8	> 8.9	3.82	28	56	16
	2B	58.7	> 7.1	3.41	31	48	21
	2A	57.5	>10	5.31	24	52	24
	1A	57.1	7.5	2.40	21	72	7
C	2C	53.4	35	9.93	—	—	—
	PP1	52.5	5.4	18.13	50	—	50
	ø	51.6	> 4.5	2.68	8	62	30
	PP2	50.7	2.9	3.24	—	—	—

* Triplet numbers are percent of sum of the three peak heights.

The first of these new characteristics is that a low (<2.5) ratio of the heights of the phenanthrene to naphthalene peaks (I and D in Fig. 1) is an excellent indication of a group A pitch. The ratio of 3.9 for pitch 4 is not as low as others, but it is still a clue that it is a more useful pitch. Petroleum-pitch 2 also has a relatively low ratio of 2.9, but it should be noted that the other characterizations will place this pitch in group C.

It was further noted that the chromatograms could be divided into three subareas that gave another secondary characterization. In the pitches in group B and C, the later regions of the chromatograms dominated the total area, but in the group A pitches the subareas of the three regions (labelled 1, 2, and 3 in Fig. 4) were approximately the same. These observations are shown quantitatively in Table IV where the subarea ratios of regions 2 to 1 are listed. A low ratio indicated a group A pitch, while a high ratio was indicative of a group B or C pitch. Again, the application of this one test was not conclusive (for example, pitches Ø and PP2).

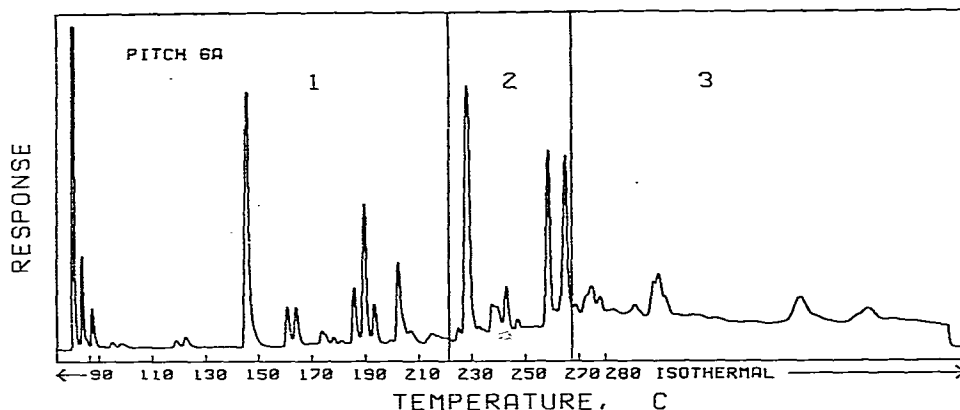Although most of our correlations were with the coking value (and thus only

Fig. 4. Three subareas of FID chromatogram used for secondary characterization.

indirectly to the other physical characteristics), we did note one correlation of potential import with respect to the quinoline insolubles. The three pitches we tested that had a low QI (2C, PP1, and PP2) gave no acenaphthylene peak. This result could be coincidental, except that a significant amount of QI is normally necessary to produce a good final electrode, and acenaphthylene itself exhibits a high degree of graphitization[20,21]. Hence, there may be some connection between these two observations.
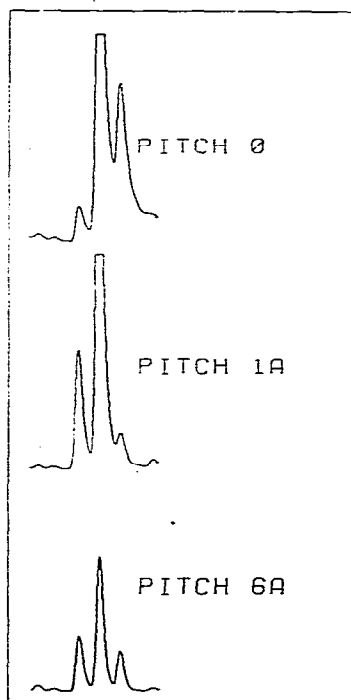
Fig. 5. Comparison of triplet peaks centered around acenaphthylene for FID plots of three coal tar-pitches.

DISCUSSION

The use of PGC for the study and characterization of such complex samples as coal tar- and petroleum-pitches appears to be promising, particularly for preliminary screening. Among the many potential advantages of this technique are the small sample (<5 mg), the rapid analysis (<2 h total time) and the ability to acquire all of the useful data in one run, as opposed to getting only one physical characteristic from each of several standard tests.

The need for more extensive testing of a variety of pitches is evident, even though we appear to have good correlations for the pitches we have studied. For example, the relationship between the presence of an acenaphthylene peak to a moderate-to-high QI value would have practical utility in screening pitches.

We have examined the use of the nitrogen detector from a qualitative viewpoint, but more extensive studies with both this and other specific detectors (in particular, a sulfur detector) could be of considerable interest with these samples. Finally, the use of pyrolysis units at higher final temperatures and various heating rates, corresponding more closely to actual graphitizing conditions, could be useful for studying the mechanisms involved in a process such as graphitization.

ACKNOWLEDGEMENTS

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